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# Enhanced $\pi$-Conjugation and Emission via Icosahedral Carboranes: Synthetic and Spectroscopic Investigation

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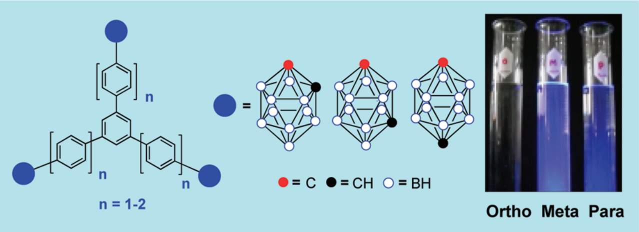
S *Supporting Information*



**ABSTRACT:** The ability of *ortho*-, *meta*- and *para*-carboranes to enhance the emission intensity has been compared. For this purpose a series of carborane-appended 1,3,5-triphenylbenzene (TB) and 1,3,5- tris(biphenyl-4-yl)benzene (TBB) containing three *ortho*-, *meta*- and *para*-carborane clusters directly attached to the conjugated cores have been synthesized employing Suzuki, Heck, and trimerization reactions. The incorporation of the icosahedral carboranes was associated with a red shift in the UV absorption spectrum of up to 13 nm as well as enhancements of the emission intensities of up to 154%. The presence of *ortho*-carboranes showed the maximum red shift in the UV spectrum whereas the maximum enhancement of the emission intensity was observed in the presence of *meta*-carborane clusters. The order of $\pi$-conjugation extension is found to be *ortho* > *meta* ≈ *para*. A comparative thermal analysis indicated *o*-carborane-appended trimers to be the most thermally stable in the series. Proton NMR spectra of reported carborane-appended trimers indicated that *ortho*- and *meta*-carborane cages have benzenelike characteristics.

## INTRODUCTION

Boron clusters, namely boranes and carboranes, possess three-center, two-electron bonds, and subsequently, three-dimensional delocalization of skeletal electrons results in a highly polarizable $\sigma$-aromatic characteristic, often referred to as three-dimensional aromaticity.[1] The unusual thermal and chemical stability of icosahedral carboranes[2] and their ability to undergo benzenelike electrophilic substitution[3] and extend $\pi$-conjugation[4] are also attributed to their aromatic properties.[5] Theoretical evidence on the aromaticity of deltahedral boranes $B_nH_n^{2-}$ ($6 \leq n \leq 12$) was given by Aihara, who found significant positive resonance energies for these clusters using a graph theoretical method. The highest resonance energy was observed for $B_{12}H_{12}^{2-}$.[6] A number of other theoretical investigations point to the existence of aromaticity in the icosahedral carboranes (Figure 1; **1**, **2**, **3**) which are isoelectronic to the $B_{12}H_{12}^{2-}$ cluster.[5] Icosahedral carboranes find a number of traditional applications such as in medicine[7] and organometallic chemistry,[8] and many new applications of boron clusters in various other areas are also emerging.[9]

The ability of icosahedral carboranes to extend $\pi$-conjugation has been exploited in synthesizing polymeric materials with improved photophysical properties. Recent reports showed that boron clusters, such as *meta*- and *para*-carboranes, are good candidates for the syntheses of light emitting polymeric materials.[4] Although the extension of $\pi$-conjugation and enhancement emission intensity via icosahedral carboranes has been reported, such properties of all three icosahedral carboranes have never been compared. Previously, we reported the synthesis and thermal and photophysical properties of *o*-carborane-appended phenylenes where the aromatic core was attached to *o*-carborane clusters via methylene moieties.[10] Thus, the enhancement of the emission intensity of the extended $\pi$-conjugated systems was attributed to the three-dimensional structure of the carborane clusters which is capable of preventing $\pi$–$\pi$ stacking interactions.[10] In this paper, we report the synthesis and thermal and photophysical properties of *ortho*-, *meta*-, and *para*-carborane-appended 1,3,5-triphenylbenzenes (TBs) and 1,3,5-tris(biphenyl-4-yl)benzenes (TBBs) where the carborane clusters are directly attached to the $\pi$-conjugated core. Symmetrical 1,3,5-phenylenebenzene core based structures TB and

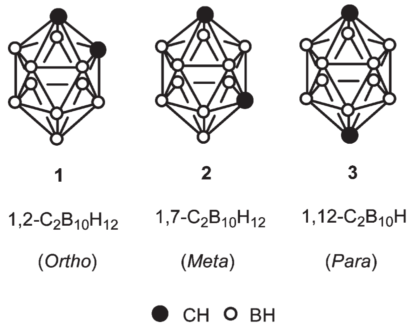


**Figure 1.** Icosahedral carboranes.

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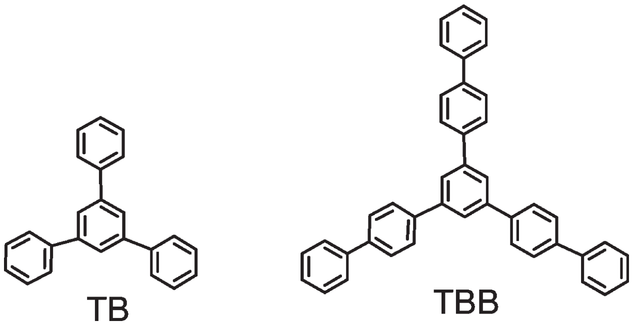
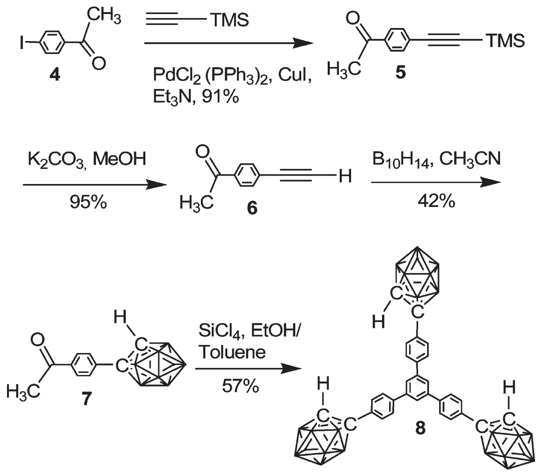
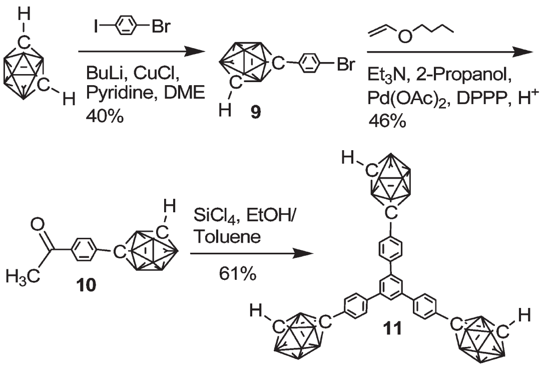


**Figure 2.** 1,3,5-Phenylenebenzenes.

**Scheme 1. Synthesis of *o*-Carborane-Appended TB**



**Scheme 2. Synthesis of *m*-Carborane-Appended TB**

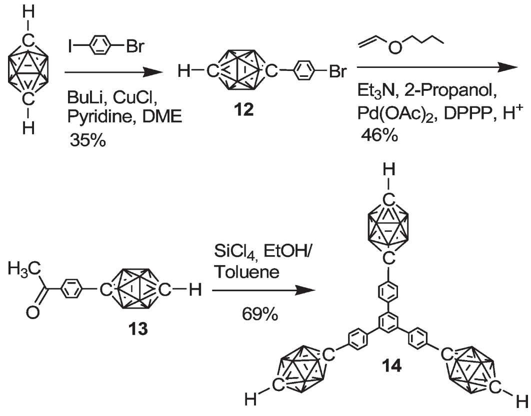


TBB, shown in Figure 2, are photostable chromophores and useful light emitting materials[11] and are often used as hole-blocking molecular materials[12a] and UV-laser dyes.[12b] The direct attachment of carborane clusters to two different $\pi$-conjugated aromatic cores gave us an opportunity to study the effect of carboranes on the photophysical properties and proton NMR splitting pattern of these $\pi$-conjugated compounds. A systematic thermal analysis of newly synthesized *o*-, *m*-, and *p*-carborane-appended trimers has also been carried out.

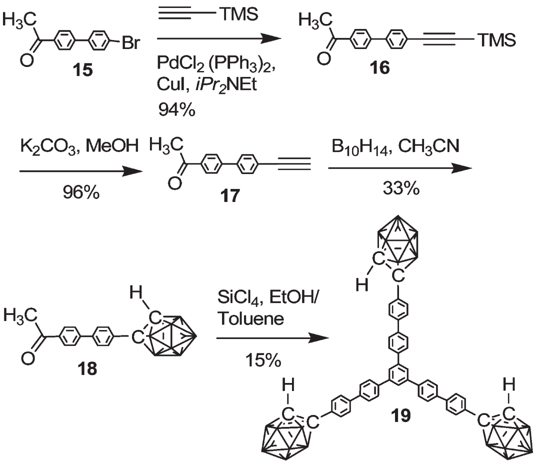
## ■ RESULTS AND DISCUSSION

**Synthesis.** The carborane C$_{cage}$-appended symmetrical trimers containing three carborane clusters were synthesized by employing palladium-catalyzed Suzuki and Sonogashira coupling reactions and palladium-catalyzed Heck reactions, followed by SiCl$_4$/ethanol mediated trimerizations[3a,10] of the formed carborane-appended aryl ketones, as shown in Schemes 1−6. Suzuki and Sonogashira coupling reactions were carried out using the common palladium catalyst PdCl$_2$(PPh$_3$)$_2$ in the presence of K$_2$CO$_3$ and Et$_3$N. The Heck reaction was carried out using catalytic amounts of Pd(OAc)$_2$ and DPPP [1,3-bis(diphenylphosphino)propane)] with butyl vinyl ether in the presence of Et$_3$N.[13] Solubility difficulties of the carborane-appended aryl ketones in ethanol were solved by adding suitable amounts of toluene to ethanol. Smaller trimers were obtained with room temperature reactions, but for the extended trimers an elevated temperature between 40 and 50 °C was required.

**Scheme 3. Synthesis of *p*-Carborane-Appended TB**

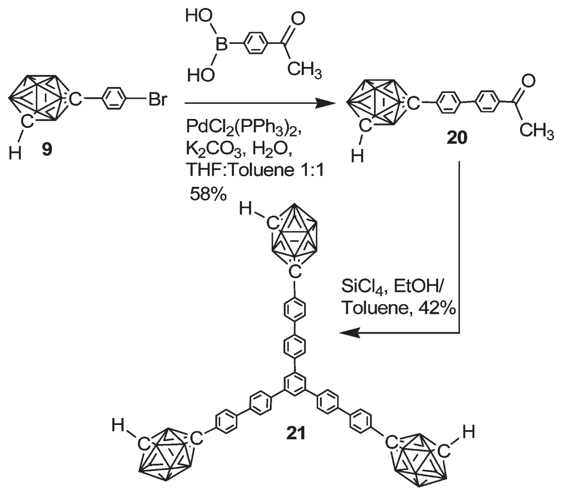


**Scheme 4. Synthesis of *o*-Carborane-Appended TBB**

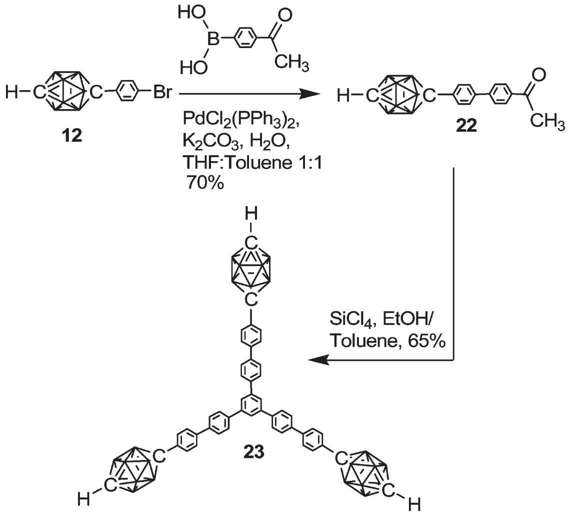


The syntheses of the carborane C$_{cage}$-appended 1,3,5-triphenylbenzene (TB) containing three *o*-carborane clusters is outlined in Scheme 1. Starting from commercially available 4-iodoacetophenone **4**, alkyne **5** was prepared via a Sonogashira coupling with ethynyltrimethylsilane followed by the deprotection of the TMS group. Alkyne **6** was then treated with the decaborane in the presence of acetonitrile to produce ketone **7** in moderate yield. Ketone **7** then underwent trimerization in the presence of SiCl$_4$/ethanol to produce the *o*-carborane-appended trimer **8**, in good yield (Scheme 1). For the syntheses of *meta*-

**Scheme 5. Synthesis of *m*-Carborane-Appended TBB**



**Scheme 6. Synthesis of *p*-Carborane-Appended TBB**



and *para*-carborane-appended trimers a different synthetic approach was employed. The C-arylated monobromo derivatives of *meta*- and *para*-carboranes, **9** and **12**, were synthesized using a reported Cu(I) mediated method[14] and purified by column chromatography and sublimation. These monobromo derivatives were then used as the starting materials for the Pd(OAc)$_2$ catalyzed Heck reactions with butyl vinyl ether in the presence of Et$_3$N and DPPP. This procedure followed by acidification resulted in the formation of ketones **10** and **13**. These *meta*- and *para*-carborane-appended ketones were then trimerized to obtain the *meta* trimer **11** and *para* trimer **14**, respectively (Schemes 2 and 3).

The attachment of carborane clusters to the extended 1,3,5-tris(biphenyl-4-yl)benzene (TBB) was carried out in a parallel manner. For the synthesis of *o*-carborane-appended trimer **19**, the commercially available ketone **15** was used as the starting compound. This underwent a palladium-catalyzed Sonogashira coupling with ethynyltrimethylsilane followed by removal of the TMS group, leading to the formation of alkyne **17**. This was then treated with decaborane, and the *o*-carborane-appended ketone **18** was formed. Ketone **18** was trimerized to afford the *o*-carborane-appended extended trimer **19** in about 15% yield (Scheme 4).

The syntheses of *meta*- and *para*-carborane-appended extended trimers were started from the respective monobromo derivatives, **9** and **12**. Compounds **9** and **12** were treated with 4-acetylphenylboronic acid under Suzuki coupling conditions to produce *meta*- and *para*-carborane-appended ketones, **20** and **22**, which were then trimerized using SiCl$_4$ to the respective *meta*- and *para*-carborane-appended extended trimers, **21** and **23**. However, the yields of *meta*- and *para*-carborane trimers **21** and **23** were higher than that for the *ortho*-carborane trimer **19** up to about 60−65% (Schemes 5 and 6). The synthesis of the control molecules, 1,3,5- triphenylbenzene (TB) and 1,3,5-tris(biphenyl-4-yl)benzene (TBB), has been described in our earlier report.[10]

**Photophysical Properties.** Light-emitting $\pi$-conjugated materials find numerous electronic applications as organic light emitting diodes, organic lasers, organic field effect transistors, and other organic devices.[15] The syntheses and photophysical properties of a number of symmetrical 1,3,5-phenylenebenzene core based structures containing multiple *o*-carborane clusters have been described in our earlier report.[10] Apart from the use of 1,3,5-tris(*p*-oligophenylene)benzenes as photostable chromophores,[10,11] hole-blocking molecular materials,[12a] and UV-laser dyes,[12b,16] the other important application of such blue light emitting materials is their use in flat-panel displays. The combination of blue, red, and green light emitting materials is essential to make the full-color flat-panel displays.[17] These materials should also possess high quantum efficiency and brightness as well as high thermal stability.[17] The use of TBB in electroluminescent (EL) devices was found to enhance the EL of the device significantly and also prevent exciplex formation.[17]

The effect of *ortho*-, *meta*-, and *para*-carboranes on the photophysical properties of TB and TBB was studied by comparing the spectroscopic properties of the carborane-appended trimers, with controls TB and TBB (see Figure 3 A,B and Table 1) in dichloromethane. The extinction coefficients ($\varepsilon_{max}$'s) of all trimers were calculated and shown in Table 1. Calculated $\varepsilon_{max}$'s of control trimers TB and TBB are consistent with the literature values.[16c,d] The carborane-appended TBs and TBBs absorb more strongly than controls, and they have larger extinction coefficients than the controls. Interestingly, the carborane-appended TBBs have increased $\varepsilon_{max}$ values compared to the carborane-appended TBs which is likely due to the decreased flexibility of the TBBs compared to the TBs. The absorption maximum for TBB was observed at 289 nm, and a red shift of 9 nm in the case of the *o*-carborane-appended TBB (**19**) and up to 8 nm for *m*- (**21**) and *p*- (**23**) carborane-appended TBBs were observed. The UV absorption spectrum of TB showed absorption maximum at 256 nm whereas the *ortho*-, *meta*-, and *para*-carborane-appended TBs (compounds **8**, **11**, and **14**) showed absorption maxima at 269, 267, and 267 nm, respectively. The red shift of 13 nm in the case of the *o*-carborane-appended TB and up to 11 nm for *m*- and *p*-carborane-appended TBs were observed. The red shift in the case of carborane-appended trimers is due to the participation of carboranes in extending the $\pi$-conjugation and in enhancing the rigidity of the system. Thus, it was found that, in both cases, the *o*-carborane-appended trimers showed the maximum red shift of up to 13 and 9 nm, respectively.

The emission spectra of TB, TBB, and all carborane-appended trimers were recorded in dichloromethane, and all these trimers were found to emit in the blue-violet region of the spectrum. Specifically, the *m*- and *p*-carborane-appended TBBs showed very strong bands in the blue-violet region. In order to measure relative fluorescence quantum yields ($\Phi_F$), TB and carborane-appended TBs were excited at 268 nm whereas the TBB and carborane-appended TBBs were excited at 290 nm. All the samples were prepared with the optical density (OD) of 0.15 which allowed us to directly compare the emission intensities.[10,18] To avoid the difficulty in determining the absolute quantum yields, a common practice is to determine the quantum yields of unknown samples by comparison with a standard of known fluorescence quantum yield.[19] The quantum yields of controls, the TB and TBB, are reported to be 0.10 and 0.27, respectively.[12b] Using these values, the relative fluorescence quantum yields ($\Phi_F$'s) of carborane-appended trimers were calculated by comparing the area under the fluorescence bands, and these values are given in Table 1. HOMO−LUMO gap energies of the controls and carborane-appended trimers were calculated and reported in eV, by using the Planck equation, from the wavelengths where the excitation and emission lines cross each other ($\lambda_c$) (Table 1). The energies for carborane-appended trimers were found to be slightly lower than the respective controls. Stokes shifts for all trimers were calculated from the excitation and emission maxima, and all trimers exhibited modest Stokes shifts of 64−82 nm (Table 1). All carborane-appended trimers exhibited lower Stokes shift compared to controls indicating that carborane-appended trimers are relatively rigid structures.[20] A lower Stokes shift was also observed for the TBBs in comparison to the TBs which is consistent with slightly greater rigidity in TBBs versus TBs. Analysis of the fluorescence spectra revealed that incorporation of *o*-carboranes that are directly attached to the TB and TBB drastically reduces the emission intensity, and the quantum yields ($\Phi_F$'s) are also reduced to only about 24% and 2.5% of the quantum yields of what was observed for TB and TBB. Therefore, very little fluorescence was observed in the case of *o*-carborane-appended trimers. However, in the case of *meta*- and *para*-carborane-appended trimers, a dramatic enhancement of the emission intensity was observed. The quantum yields of *m*- and *p*-carborane-appended TBs are enhanced up to the extent of 154% and 133% of the $\Phi_F$ of TB. The $\Phi_F$ of the *m*-carborane-appended TB is enhanced to such a proportion that it can now be comparable to the $\Phi_F$ of TBB. The quantum yields of *m*- and *p*-carborane-appended TBBs are also enhanced up to the extent of 74% and 33% of the $\Phi_F$ of the TBB. The $\Phi_F$ of the *m*-carborane-appended TBB is slightly more than the previously reported compound that contains six *o*-carboranes appended to the TBB core via methylene moeties[10] and the $\Phi_F$ of the *p*-carborane-appended TBB is slightly more than the previously reported compound which contains three *o*-carboranes appended to the TBB core via methylene moeties.[10]

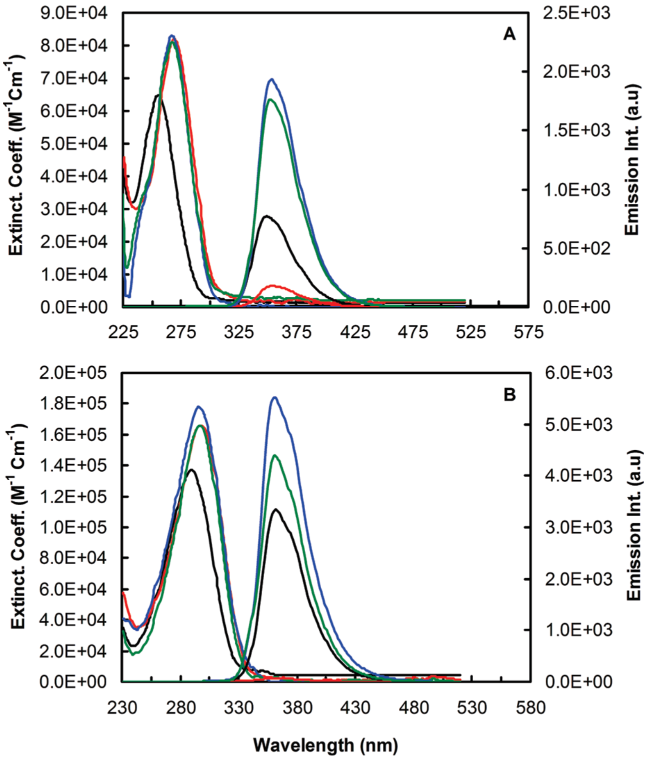


**Figure 3.** (A) Absorption and emission spectra of carborane-appended TB in dichloromethane at room temperature: red, *ortho* (**8**); blue, *meta* (**11**); green, *para* (**14**); black, TB. (B) Absorption and emission spectra of carborane-appended TBB in dichloromethane at room temperature: red, *ortho* (**19**); blue, *meta* (**21**); green, *para* (**23**); black, TBB.

Fluorescence quenching in the *o*-carborane-appended TB and TBB is in accordance with the observation of Kokado and coworkers who found that the introduction of *o*-carboranes in the extended $\pi$-systems of *p*-phenylene-ethynyl-like polymers resulted in a similar effect and no luminescence was observed.[4b,c] Intramolecular charge transfer from electron-donating $\pi$-conjugated core to the antibonding orbital of C−C bond of *o*-carboranes has been attributed to such an effect.[4b] On the other hand, reports on *m*- and *p*-carborane containing polymers revealed that they contribute positively to the photophysical properties of $\pi$-conjugated polymers.[4] In the present study, we also observed that *m*- and *p*-carborane-appended TBs and TBBs showed a dramatic enhancement of fluorescence intensity which can be explained on the basis of the three-dimensional (3D) structure of

**Table 1. Spectroscopic Data of Carborane-Appended TB and TBB**[a]

| trimer | abs max, $\lambda_{max}$ (nm) | emission max (nm) | extinct coeff, $\varepsilon$ ($M^{-1}cm^{-1}$) | Stokes shift (nm) | relative area | quantum yield, $\Phi_F$ | *E* (eV) |
|---|---|---|---|---|---|---|---|
| TB | 256 | 349 | 65 000 ± 1600 | 82 | 1.0 | 0.10 | 3.838 |
| 8 | 269 | 355 | 82 000 ± 2600 | 79 | 0.242 | 0.024 | 3.815 |
| 11 | 267 | 353 | 83 000 ± 2100 | 78 | 2.540 | 0.254 | 3.827 |
| 14 | 267 | 352 | 81 000 ± 2500 | 77 | 2.337 | 0.233 | 3.827 |
| TBB | 289 | 362 | 137 000 ± 3300 | 72 | 1.0 | 0.27 | 3.723 |
| 19 | 298 | 361 | 166 000 ± 860 | 64 | 0.025 | 0.0068 | 3.712 |
| 21 | 297 | 361 | 178 000 ± 2500 | 64 | 1.738 | 0.469 | 3.712 |
| 23 | 297 | 361 | 166 000 ± 1300 | 65 | 1.332 | 0.359 | 3.712 |

[a] All measurements made in dichloromethane.

**Table 2. 10% Mass Loss Temperatures from TG Analysis**

| trimers | temperature (°C) |
|---|---|
| 8 | 365 |
| 11 | 355 |
| 14 | 260 |
| 19 | 522 |
| 21 | 510 |
| 23 | 503 |

icosahedral carboranes.[21] The 3D structure prevents the $\pi-\pi$ stacking interactions in the $\pi$-conjugated systems and enhances rigidity of the conjugated molecules. This was observed in the case of *o*-carborane-appended TBBs in our previous work.[10] In addition, we also observed that *m*-carborane was found to be the best among the three icosahedral carboranes in enhancing emission intensity of $\pi$-conjugated systems. The highest red shifts in the absorption spectra up to 13 and 9 nm were observed for *o*-carborane-appended TB and TBB, respectively. However, for the *meta*- and *para*-carborane-appended TBs the red shifts in the absorption spectra were reduced to 11 nm, and for the *meta*- and *para*-carborane-appended TBBs it was found to be 8 nm. Although the observed difference is small, up to 1−2 nm, in both the cases the highest $\pi$-conjugation extension is observed in the case of *o*-carborane-appended systems. A similar trend was also observed in the case of emission spectra of carborane-appended TBs. A number of other observations indicate the passage of electronic communication through carborane clusters. For example, *para*-carborane clusters have been found to transmit electronic communication between metal centers in different metal complexes.[22] Investigations on various *p*-carborane derivatives have led to a conclusion that *p*-carborane transmits an electronic effect similar to that of a formal unsaturated system.[23] The *o*-carborane derivatives are found to show weak *exo*-dative $\pi$-bonding.[24] Electronic communication between substituent groups on the cage carbon and other cage atoms of *o*-carborane derivatives has also been observed.[25] All such effects have been routinely verified using spectroscopic, cyclic voltametric, crystallographic, and computational studies and solvolysis experiments.[26]

**Thermal Properties.** It has been found that molecules containing multiple carborane clusters are thermally very stable.[19] We observed in our previous report that for $\pi$-conjugated compounds containing multiple *o*-carborane clusters 10% mass loss occurred close to 500 °C.[10] Recently reported large dendrimers containing up to 81 carborane clusters were also found to be stable up to 400 °C.[9a] To assess and compare the thermal properties of the newly synthesized carborane-appended trimers a systematic thermal analysis was carried out. The 10% mass loss temperature data of all trimers have been summarized in Table 2. In the case of the small trimer series *o*-carborane-appended small trimer **8** was found to be the most thermally stable with the 10% mass loss temperature found to be 365 °C and about 20% of the residue was maintained at 700 °C. But 10% mass loss temperatures were found to be 355 and 260 °C for *meta* (**11**) and *para* (**14**) carborane-appended small trimers, respectively. However, for both the cases only a negligible mass of the residue (about 3%) remained at 700 °C. The larger trimers were found to be more thermally stable, and the 10% mass loss temperatures were found to be 522 °C (for the *o*-carborane-appended trimer **19**), 510 °C (for the *m*-carborane-appended trimer **21**), and 503 °C (for the *p*-carborane-appended trimer **23**), respectively. In the case of extended trimers a large amount of the residue (about 55−59 wt %) was found to be maintained at 700 °C (Figure 4).

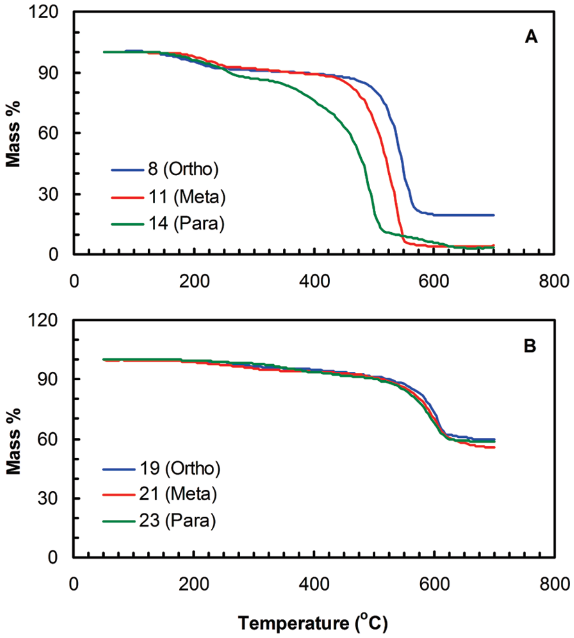


**Figure 4.** (A) TGA curves of small trimers under argon. (B) TGA curves of extended trimers under argon.

So, in both the cases *o*-carborane-appended trimers were found to be the most thermally stable followed by the *meta*- and *para*-carborane-appended trimers. The lowest thermal stability was observed in the case of *para*-carborane-appended small trimer (**14**). This may be because of the tendency of the *p*-carboranes to easily get sublimed. However, it is found that all these carborane-appended trimers show significantly higher thermal stability as 10% mass loss temperatures for carborane unsubstituted phenylene cores were found to be lower (257 °C for TB and 210 °C TBB).[10]

**NMR.** All carborane containing trimers have been characterized by NMR, and confirmatory mass spectral analysis has been carried out. Multinuclear NMR data for all compounds reported here are given in the Experimental Section, and NMR spectra of all compounds are shown in the Supporting Information (SI). The difference in the electronic properties among the icosahedral carboranes has been reflected in the splitting pattern of the proton NMR spectra of *o*-, *m*-, and *p*-carborane trimers. Therefore, the salient features of the proton NMR splitting pattern of conjugated carborane-appended trimers deserve brief mention. The *ortho* trimer **8** and *meta* trimer **11** in the small trimer series showed singlets for the 12 peripheral aromatic protons at 7.63 and 7.55 ppm, respectively. However, in the case of *para* trimer **14** these peripheral aromatic protons were observed as two doublets at 7.44 and 7.31 ppm, respectively, with coupling constant (*J*) 8.5 Hz. A similar splitting pattern was also observed in the NMR spectra of extended carborane-appended trimers, and the 12 peripheral aromatic protons in the *ortho*-carborane containing extended trimer (**19**) were observed as two very closely placed doublets at 7.65 and 7.61 ppm having *J* values of 9 and 8.50 Hz, respectively (see SI). Similarly, the 12 peripheral aromatic protons of the *m*-carborane containing extended trimer **21** also showed two closely placed doublets at 7.58 and 7.55 ppm with *J* value of 9.0 Hz. In both the cases of *o*- and *m*-carborane-appended extended trimers (**19** and **21**), it was observed that the signals from the 12 peripheral aromatic protons are gradually merging to appear as one doublet. However, well separated doublets, at 7.48 and 7.33 ppm with *J* value 8.5 Hz, were observed for the 12 peripheral aromatic protons of the *p*-carborane-appended extended trimer **23**. Such a similarity in the splitting pattern in proton NMR spectra of both *o*- and *m*-carborane-appended species indicated that the carborane cages have benzenelike characteristics. However, in the case of the *p*-carborane-appended trimers, a different proton NMR splitting pattern was observed and thus it does not seem to possess characteristics similar to that of the *o*- and *m*-carborane clusters. A similar splitting pattern was also observed for the carborane-appended extended keto precursors (see SI). The NMR spectroscopic evidence in support of electronic communication through icosahedral carboranes has been well documented in literature reports.[23−25] Boron NMR studies on the *o*-carborane derivatives revealed that the substituent at $C_1$ affected the antipodal $B_{12}$ boron shift.[24] In another report it has been found that the antipodal $B_{12}$ boron shift is also associated with a stronger *exo*-$\pi$-bond at $C_1$.[25] Unequivocal evidence for electronic interaction, involving transfer of electron density from a C-aryl group to the antipodal carbon atom of the *p*-carborane cage, has been found from the $^{13}$C NMR spectra of mono- and diaryl-*p*-carboranes.[23]

## ■ CONCLUSION

The synthesis, spectroscopic and thermal properties, and NMR splitting pattern of novel carborane-appended 1,3,5-phenylenes and oligo-phenylenes containing three *ortho*-, *meta*-, and *para*-carborane clusters directly attached to the $\pi$-conjugated core have been described. The UV absorption spectrum of all carborane-appended trimers showed a red shift indicating the involvement of carboranes in extending the $\pi$-conjugation. The maximum red shift in the absorption and emission spectrum is observed in the *o*-carborane-appended trimers followed by *m*- and *p*-carborane-appended trimers. The carborane-appended TBs and TBBs also have larger extinction coefficients than the controls. The presence of *m*- and *p*-carboranes dramatically enhanced the emission intensity with the largest change being observed for the *m*-carborane-appended trimers. However, the presence of *o*-carborane directly linked to the $\pi$-conjugated systems induces fluorescence quenching, and the emission intensity of the *o*-carborane-appended trimers diminishes. Thermal gravimetric analysis of carborane-appended trimers showed *o*-carborane-appended trimers to be the most thermally stable. Proton NMR spectra of carborane-appended trimers revealed that *o*- and *m*-carboranes do possess benzenelike characteristics.

## ■ 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 using Bruker Fourier transform multinuclear NMR spectrometer at 500.13 and 125.75 MHz, respectively. Chemical shifts are reported relative to TMS ($^1$H: $\delta$ = 0.00 ppm), $CDCl_3$ ($^{13}$C: $\delta$ = 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 and 160.5 MHz relative to $BF_3 \cdot Et_2O$. Infrared spectra were recorded using an ATI Mattson Genesis series FT-IR spectrophotometer. Elemental analyses were carried out with the CHN-Analyzer 2400 (Perkin-Elmer). Melting points were measured with a Mel-Temp II apparatus (Laboratory Devices) 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. UV absorption and emission spectra were measured with the Perkin-Elmer Lambda XLS+ UV−vis spectrometer and the Hitachi F-2500 fluorescence spectrophotometer, respectively. Mass spectral analyses were performed with the Applied Biosystems Voyager-DE STR-MALDI-TOF spectrometer, the Waters Q-TOF Ultima ES spectrometer, and VSE-70 EI mass spectrometer.

**Preparations and Analytical Data of Compounds.** *Compound **5***. Commercially available compound **4** (5 g, 20.32 mmol) was dissolved in 50 mL of dry THF. $Et_3N$ (50 mL), $PdCl_2$ $(PPh_3)_2$ (285 mg, 2 mol %), CuI (78 mg, 2 mol %), and trimethyl silyl acetylene (4.5 mL) were added to it at room temperature. The reaction mixture was stirred at room temperature for 24 h and then filtered over a silica gel pad. After evaporation of the solvent the crude reaction mixture was purified by silica gel column chromatography with 10−15% ethyl acetate in hexane as eluent to obtain 5.42 g of pure compound **5** as a colorless liquid. Yield: 91%. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.90 (d, 2H, *J* = 7.65 Hz), 7.55 (d, 2H, *J* = 7.6 Hz), 2.61 (s, 3H, $CH_3$), 0.28 (s, 9H, $SiMe_3$). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 197.2, 136.4, 132.0, 128.0, 127.9, 104.0, 98.1, 26.5, −0.1. IR (neat): 2961, 2159, 1687, 1600, 1401, 1264, 864 cm$^{-1}$. $C_{13}H_{16}OSi$: C 72.17, H 7.45. Found: C 72.11, H 7.44. ES-MS (*m*/*z*): calcd 216.35, found 217.1 ($M^+$ + 1, 100%).

*Compound **6***. Compound **5** (5.42 g, 25.0 mmol) was dissolved in 50 mL of THF and 50 mL of MeOH. Then, $K_2CO_3$ (5.17 g, 37.5 mmol) was added to it, and the mixture was stirred at room temperature for 4 h. The reaction mixture was quenched with saturated ammonium chloride solution, and then the crude reaction mixture was extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$. After evaporation of the solvent the crude reaction mixture was purified by silica gel column chromatography with 10−15% ethyl acetate in hexane as eluent to obtain 3.4 g of pure compound **6** as a colorless solid. Yield: 95%. Mp: 61 °C. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.92 (d, 2H, *J* = 6.90 Hz), 7.59 (d, 2H, *J* = 6.95 Hz), 3.27 (s, 1H), 2.61 (s, 3H, $CH_3$).$^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 197.2, 136.7, 132.2, 128.1, 126.9, 82.7, 80.3, 26.6. IR (KBr): 3211, 3016, 2097, 1671, 1598, 1400, 1261, 1171, 958, 827 cm$^{-1}$. $C_{10}H_{18}O$ calcd: C 83.31, H 5.59. Found: C 83.33, H 5.58. EI-MS (*m*/*z*): calcd 144.17, found 144.1 ($M^+$, 100%).

*Ketone **7***. Decaborane (2.769 g, 22.65 mmol) was refluxed in acetonitrile (50 mL) for 1 h. The reaction mixture was allowed to cool to room temperature, and then compound **6** (3.2 g, 22.2 mmol) in dry acetonitrile (20 mL) was added to the reaction mixture. Again it was refluxed at 90−100 °C for 6 h. The reaction mixture was then filtered through a cotton plug and concentrated. The crude reaction mixture was purified by silica gel column chromatography with 10% ethyl acetate in hexane as eluent to obtain 2.5 g of pure compound **7** as a colorless solid. Yield: 42%. Mp: 100 °C. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.93 (d, 2H, *J* = 8.5 Hz), 7.60 (d, 2H, *J* = 8.5 Hz), 4.0 (s, 1H, cage-H), 2.62 (s, 3H, $CH_3$).$^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 196.7, 137.9, 137.8, 128.6, 127.7, 75.3, 59.7, 26.7. $^{11}$B NMR (proton decoupled, 64.2 MHz): −1.89, −3.67, −8.59, −10.82. IR (KBr): 3060, 2597, 1683, 1605, 1405, 1359, 1270, 1074, 1022, 841 cm$^{-1}$. $C_{10}B_{10}H_{18}O$ calcd: C 45.78, H 6.92. Found: C 45.76, H 6.90. ES-MS (*m*/*z*): calcd 262.359, found 263.24 ($M^+$ + 1, 100%).

*Trimer **8***. Ketone **7** (1.1 g, 4.19 mmol) was solubilized in 24 mL of solvent (absolute ethanol/toluene 3:1). Then, $SiCl_4$ (7.2 mL, 62.89 mmol) was added to it at room temperature, and it was stirred at room temperature for 20 h. The reaction mixture was quenched with water and extracted with dichloromethane. Purification of the compound with silica gel column chromatography with 5−20% ethyl acetate in hexanes as eluent resulted in 700 mg of pure product **8** as colorless solid. Yield: 69%. Mp: >260 °C. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.73 (s, 3H), 7.63 (s, 12H), 4.0 (s, 3H, cage-H). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 142.1, 141.1, 133.1, 128.2, 127.6, 125.6, 76.0, 60.1. $^{11}$B NMR (proton decoupled, 64.2 MHz): −1.92, −8.82, −10.70. IR (KBr): 3069, 2924, 2593, 1594, 1511, 1393, 1072, 838 cm$^{-1}$. $C_{30}B_{30}H_{48}$ calcd: C 49.15, H 6.60. Found: C 49.14, H 6.58. ES-MS (*m*/*z*): calcd 733.03, found 732.7 ($M^+$, 100%).

*Compound* ***9***. BuLi (16 mL, 25.52 mmol) was added to the solution of *meta*-carborane (3.5 g, 24.30 mmol) in anhydrous DME (100 mL) at 0 °C, and it was stirred for 30 min at 0 °C. Then, CuCl (3.12 g, 31.59 mmol) was added to it in one portion, and it was stirred at room temperature for another 30 min. Then, pyridine (18 mL, 218.7 mmol) followed by 1-bromo-4-iodobenzene (7.22 g, 25.52 mmol) was added to it. It was refluxed for 72 h at 95−100 °C. After that, 150 mL of diethyl ether was added to the reaction mixture, and the black Cu−Py complex precipitate was filtered. The organic layer was washed with 150 mL of 2.5 M HCl and dried with $MgSO_4$. After evaporation of the solvent the crude compound was first purified by column chromatography using hexane as eluent. This mixture was further purified by sublimation. The unreacted *meta*-carborane was recovered at 50 °C, and then it was further sublimed at 70−80 °C to obtain pure compound **9**. Yield: 2.9 g, 40%. Mp: 60 °C. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.41 (d, 2H, *J* = 8.80 Hz), 7.31 (d, 2H, *J* = 8.70 Hz), 3.0 (s, 1H, cage-H). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 134.2, 131.5, 129.4, 123.2, 55.2. $^{11}$B NMR (proton decoupled, 64.2 MHz): −3.91, −10.28, −13.22, −15.0. IR (KBr): 3057, 2604, 2559, 1491, 1397, 1075, 1011,875 cm$^{-1}$. $C_8B_{10}H_{15}Br$ calcd: C 32.11, H 5.05. Found: C 32.13, H 5.01. ES-MS (*m*/*z*): calcd 299.218, found 299.2 ($M^+$, 100%).

*Ketone* ***10***. To a solution of compound **9** (750 mg, 2.5 mmol) in 2-propanol (5 mL) were added butyl vinyl ether (1.12 mL, 8.75 mmol), triethylamine (0.9 mL), $Pd(OAc)_2$ (28 mg, 5 mol %), and DPPP (82.5 mg, 8 mol %). Then, the reaction mixture was refluxed at 120 °C for 36 h. The reaction mixture was cooled to room temperature, and then 5% HCl (20 mL) was added to it, followed by stirring for 15 min at room temperature, extracting with dichloromethane thrice, and drying the combined organic layers over $MgSO_4$. After evaporation of the solvent, the residue was purified by silica gel column chromatography with 5% ethyl acetate in hexanes as the eluent to obtain 300 mg of pure compound **10** as a colorless solid, yield 46%. Mp: 110 °C. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.86 (d, 2H, *J* = 9.0 Hz), 7.54 (d, 2H, *J* = 8.5 Hz), 3.13 (s, 1H, cage-H), 2.59 (s, 3H, $CH_3$). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 197.1, 139.7, 137.0, 128.3, 128.2, 55.2, 26.6. $^{11}$B NMR (proton decoupled, 160.5 MHz): −3.92, −8.20, −10.29, −13.20, −15.11. IR (KBr): 3062, 2604, 2568, 1689, 1600, 1402, 1381, 1268, 849 cm$^{-1}$. $C_{10}B_{10}H_{18}O$ calcd: C 45.78, H 6.92. Found: C 45.76, H 6.91. ES-MS (*m*/*z*): calcd 262.359, found 262.2 ($M^+$, 100%).

*Trimer* ***11***. Ketone **10** (140 mg, 0.533 mmol) was solubilized in 6 mL of solvent (absolute ethanol/toluene 3:1). Then $SiCl_4$ (1.22 mL, 10.67 mmol) was added to it at room temperature, and it was stirred at room temperature for 15 h. Purification of the compound with silica gel column chromatography using hexanes as eluent resulted in 80 mg of pure product **11** as colorless solid. Yield: 61%. Mp: >260 °C. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.70 (s, 3H), 7.55 (s, 12H), 3.13 (s, 3H, cage-H). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 141.3, 141.1, 134.7, 128.4, 127.1, 125.3, 77.9, 55.1. $^{11}$B NMR (proton decoupled, 160.5 MHz): −3.83, −10.3, −13.2, −15.0., −15.0. IR (KBr): 3071, 2923, 2601, 1590, 1513, 1394, 1080, 1040, 909, 845 cm$^{-1}$. $C_{30}B_{30}H_{48}$ calcd: C 49.15, H 6.60. Found: C 49.13, H 6.54. ES-MS (*m*/*z*): calcd 733.03, found 732.3 ($M^+ - 1$, 100%).

*Compound* ***12***. BuLi (16 mL, 25.52 mmol) was added to the solution of *para*-carborane (3.5 g, 24.30 mmol) in DME (100 mL) at 0 °C, and the mixture was stirred for 30 min at 0 °C. Then, CuCl (3.12 g, 31.59 mmol) was added in one portion, and then it was stirred at room temperature for another 30 min. Then, pyridine (18 mL, 218.7 mmol) was added to it followed by 7.22 g (25.52 mmol) of 1-bromo-4-iodobenzene. It was then refluxed for 72 h at 95−100 °C, and diethyl ether was added to the reaction mixture. The black precipitate Cu−Py complex which formed was allowed to settle down and was then filtered off. The organic layer (filtrate) was washed with 150 mL of 2.5 M HCl and dried with $MgSO_4$. After evaporation of the solvent the crude compound was first purified by silica gel column chromatography using hexane as the eluent. The resulting mixture was further purified by sublimation. The unreacted *para*-carborane was first recovered at 50 °C, and then the fraction obtained at 70 °C was again purified using silica gel column chromatography using hexane as eluent to get pure compound **12**. Yield: 2.5 g, 35%. Mp: 90 °C. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.32 (d, 2H, *J* = 8.46 Hz), 7.09 (d, 2H, *J* = 8.51 Hz), 2.82 (s, 1H, cage-H). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 135.8, 131.1, 128.7, 122.8, 77.5, 59.9. $^{11}$B NMR (proton decoupled, 64.2 MHz): −12.38, −14.88. IR (KBr): 3060, 2611, 1900, 1492, 1396, 1074, 1008, 894, 848, 802 cm$^{-1}$. $C_8B_{10}H_{15}Br$ calcd: C 32.11, H 5.05. Found: C 32.12, H 5.01. ES-MS (*m*/*z*): calcd 299.21, found 299.1 ($M^+$, 100%).

*Ketone* ***13***. To a solution of compound **12** (750 mg, 2.5 mmol) in 2-propanol (5 mL) were added butyl vinyl ether (1.12 mL, 8.75 mmol), triethyl amine (0.9 mL), $Pd(OAc)_2$ (28 mg, 5 mol %), and DPPP (82.5 mg, 8 mol %). The reaction mixture was then refluxed at 120 °C for 36 h and allowed to cool to room temperature. A 5% HCl (20 mL) was then added to it, and the resultant mixture was stirred for 15 min at room temperature and extracted with dichloromethane thrice. 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% ethyl acetate in hexanes as the eluent to obtain 300 mg of pure compound **13** as a colorless solid, yield 46%. Mp: 140 °C. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.78 (d, 2H, *J* = 8.5 Hz), 7.33 (d, 2H, *J* = 8.50 Hz), 2.85 (s, 1H, cage-H), 2.56 (s, 3H, $CH_3$). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 197.2, 141.2, 136.7, 128.0, 127.4, 85.3, 60.4, 26.6. $^{11}$B NMR (proton decoupled, 160.5 MHz): −12.39, −14.84. IR (KBr): 3008, 2924, 2616, 1685, 1599, 1382, 1254, 815 cm$^{-1}$. $C_{10}B_{10}H_{18}O$ calcd: C 45.78, H 6.92. Found C 45.73, H 6.91. ES-MS (*m*/*z*): calcd 262.35, found 262.2 ($M^+$, 100%).

*Trimer* ***14***. Ketone **13** (120 mg, 0.457 mmol) was solubilized in 6 mL of solvent (absolute ethanol/toluene 3:1). Then, $SiCl_4$ (1.05 mL, 9.147 mmol) was added to it at room temperature, and then it was stirred at room temperature for 15 h. Purification of the compound with silica gel column chromatography with hexanes as eluent resulted in 80 mg of pure product **14** as colorless solid. Yield: 69%. Mp: >260 °C. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 7.6 (s, 3H), 7.44 (d, 6H, *J* = 8.50 Hz), 7.31 (d, 6H, *J* = 8.50 Hz), 2.83 (s, 3H, cage-H). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 141.2, 140.7, 136.3, 127.5, 126.8, 125.1, 86.1, 59.8. $^{11}$B NMR (proton decoupled, 160.5 MHz): −12.30, −14.93. IR (KBr): 3062, 2957, 2930, 2610, 1509, 1399, 1260, 1090, 850 cm$^{-1}$. $C_{30}B_{30}H_{48}$ calcd: C 49.15, H 6.60. Found: C 49.11, H 6.58. ES-MS (*m*/*z*): calcd 733.03, found 732.6 ($M^+$, 100%).

*Compound* ***16***. Compound **15** (1 g, 3.634 mmol) was dissolved in 20 mL of dry THF. Then, *i*$Pr_2NEt$ (5.8 mL), $Pd(PPh_3)_4$ (210 mg, 5 mol %), CuI (35 mg, 5 mol %), and trimethyl silyl acetylene (2.5 mL, 18.17 mmol) were added at room temperature. The mixture was stirred at 60 °C for 20 h and then filtered over a silica gel pad. After evaporation of the solvent, the crude reaction mixture was purified by silica gel column chromatography with 10% ethyl acetate in hexane as eluent to obtain 1.05 g of pure compound **16** as a colorless solid. Yield: 94%. Mp: 120 °C. $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ 8.05 (d, 2H, *J* = 8.45 Hz), 7.70 (d, 2H, *J* = 8.40 Hz), 7.59 (d, 4H, *J* = 2.35 Hz), 2.66 (s, 3H, $CH_3$), 0.29 (s, 9H, $SiMe_3$). $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ 197.5, 144.7, 139.7, 136.1, 132.5, 128.9, 127.1, 127.0, 123.1, 104.6, 95.6, 26.6, −0.03. IR (KBr): 2960, 2902, 2160, 1687, 1600, 1397, 1360, 1262, 1199, 957, 846 cm$^{-1}$. $C_{19}H_{20}OSi$ calcd: C 78.03, H 6.89. Found: C 78.02, H 6.87. ES-MS (*m*/*z*): calcd 292.45, found 293.1 ($M^+ + 1$, 100%).

*Compound* ***17***. Compound **16** (730 mg, 2.496 mmol) was dissolved in 10 mL of THF and 10 mL of MeOH. Then, $K_2CO_3$ (379 mg, 2.745 mmol) was added to it, and the mixture was stirred at room temperature for 5 h. The reaction mixture was quenched with saturated ammonium chloride solution, and then the crude reaction mixture was extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$. After evaporation of the solvent the crude reaction mixture was purified by silica gel column chromatography with 10% ethyl acetate in hexane as eluent to obtain 400 mg of pure compound **17** as a colorless solid. Yield: 72%. Mp: 150 °C. $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 8.07 (d, 2H, $J$ = 8.45 Hz), 7.71 (d, 2H, $J$ = 8.50 Hz), 7.62 (s, 4H), 3.18 (s, 1H), 2.66 (s, 3H, $CH_3$).$^{13}C$ NMR ($CDCl_3$, 125 MHz): $\delta$ 197.6, 144.7, 140.1, 136.2, 132.7, 128.9, 127.1, 122.0, 83.2, 78.3, 26.6. IR (KBr): 3215, 2098, 1670, 1601, 1397, 1270, 955, 817 $cm^{-1}$. $C_{16}H_{12}O$ calcd: C 87.25, H 5.49. Found: C 87.23, H 5.50. ES-MS ($m/z$): calcd 220.27; found 221.1 ($M^+ + 1$, 100%).

*Ketone* ***18***. Decaborane (244 mg, 1.997 mmol) was refluxed in acetonitrile (10 mL) for 3 h. Then, the reaction mixture was cooled to room temperature, and then compound **17** (400 mg, 1.816 mmol) in toluene (3 mL) was added to the reaction mixture. Again it was refluxed at 90−100 °C for 20 h. Then, the reaction mixture was filtered through a cotton plug, and then the organic portion was concentrated. The crude reaction mixture was purified by silica gel column chromatography with 10% ethyl acetate in hexane as eluent to obtain 200 mg of pure compound **18** as a colorless solid. Yield: 33%. Mp: 170 °C. $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 8.07 (d, 2H, $J$ = 8.50 Hz), 7.66 (d, 2H, $J$ = 8.0 Hz), 7.68 (s, 4H), 4.04 (br, s, 1H, cage-H), 2.66 (s, 3H, $CH_3$).$^{13}C$ NMR ($CDCl_3$, 125 MHz): $\delta$ 197.5, 144.8, 141.5, 136.5, 133.3, 129.0, 128.2, 127.6, 127.2, 76.0 ($C_{cage}$), 60.1 ($C_{cage}$), 26.6. $^{11}B$ NMR (proton decoupled 160.5 MHz): −1.89, −4.10, −8.82, −10.79, −12.59. IR (KBr): 3066, 2585, 1296, 1672, 1603, 1522, 1395, 1355, 1266, 1002, 824 $cm^{-1}$. $C_{16}H_{22}B_{10}O$ calcd: C 56.78, H 6.55. Found: C 56.74, H 6.55. MALDI-TOF-MS ($m/z$): calcd 338.45, found 338.66 ($M^+$, 100%).

*Trimer* ***19***. Ketone **18** (930 mg, 2.747 mmol) was solubilized in 45 mL of solvent (absolute ethanol/toluene 3:1). Then, $SiCl_4$ (9.5 mL, 82.43 mmol) was added to it at room temperature, and then it was stirred at 50 °C temperature for 24 h. The reaction mixture was quenched with water and extracted with dichloromethane. Purification of the compound with silica gel column chromatography with 5−20% ethyl acetate in hexanes as eluent resulted in 130 mg of pure product **19** as a colorless solid. Yield: 15%. Mp: >260 °C. $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 7.90 (s, 3H), 7.83 (d, 6H, $J$ = 8.50 Hz), 7.72 (d, 6H, $J$ = 8.50 Hz), 7.63 (d, 6H, $J$ = 9.0 Hz), 7.61 (d, 6H, $J$ = 8.50 Hz), 4.03 (br, s, 3H, cage-H). $^{13}C$ NMR ($CDCl_3$, 125 MHz): $\delta$ 142.2, 141.8, 140.7, 138.7, 132.6, 128.1, 127.9, 127.6, 127.3, 125.2, 77.5 ($C_{cage}$), 76.2 ($C_{cage}$). $^{11}B$ NMR (proton decoupled, 160.5 MHz): −1.92, −8.89, −10.79. IR (KBr): 3061, 2923, 2852, 2595, 1596, 1498, 1391, 1260, 1073, 1004, 823 $cm^{-1}$. $C_{48}H_{60}B_{30}$ calcd: C 59.97, H 6.29. Found: C 59.96, H 6.31. MALDI-TOF-MS ($m/z$): calcd 961.32, found 961.52 ($M^+$, 100%).

*Ketone* ***20***. Compound **9** (500 mg, 1.67 mmol) was dissolved in 20 mL of solvent (THF/toluene, 1:1). Then, 4-acetylphenylboronic acid (548 mg, 3.34 mmol), $PdCl_2(PPh_3)_2$ (47 mg, 4 mol %), and a solution of $K_2CO_3$ (691 mg, 5.01 mmol) in 3 mL of distilled water were added to it. It was refluxed at 100 °C for 24 h and then extracted with dichloromethane thrice, 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 10−15% ethyl acetate in hexanes as the eluent to obtain 330 mg of pure compound **20** as a colorless solid, yield 58%. Mp: 140 °C. $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 8.06 (d, 2H, $J$ = 8.44 Hz), 7.66 (d, 2H, $J$ = 8.43 Hz), 7.54 (s, 4H), 3.12 (br, s, 1H, cage-H), 2.66 (s, 3H, $CH_3$). $^{13}C$ NMR ($CDCl_3$, 125 MHz): $\delta$ 197.5, 144.3, 140.2, 136.2, 135.1, 129.0, 128.4, 127.1, 77.8 ($C_{cage}$), 55.1 ($C_{cage}$), 26.6. $^{11}B$ NMR (proton decoupled, 160.5 MHz): −3.86, −8.52, −10.32, −13.28, −15.06. IR (KBr): 3059, 3036, 2604, 1683, 1602, 1394, 1267, 1080, 818 $cm^{-1}$. $C_{16}H_{22}B_{10}O$ calcd: C 56.78, H 6.55. Found: C 56.72, H 6.55. MALDI-TOF-MS ($m/z$): calcd 338.45, found 338.62 ($M^+$, 100%).

*Trimer* ***21***. Ketone **20** (250 mg, 0.738 mmol) was solubilized in 15 mL of solvent (absolute ethanol/toluene 3:1). Then, $SiCl_4$ (2.5 mL, 22.16 mmol) was added to it at room temperature, and it was stirred at 50 °C for 24 h. Purification of the compound with silica gel column chromatography with 5−10% ethyl acetate in hexanes as eluent resulted in 100 mg of pure product **21** as colorless solid. Yield: 42%. Mp: >260 °C. $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 7.89 (s, 3H), 7.81 (d, 6H, $J$ = 8.50 Hz), 7.70 (d, 6H, $J$ = 8.50 Hz), 7.56 (d, 6H, $J$ = 9.0 Hz), 3.1 (br, s, 3H, cage-H). $^{13}C$ NMR ($CDCl_3$, 125 MHz): $\delta$ 141.8, 141.0, 140.3, 139.1, 134.3, 128.3, 127.8, 127.5, 126.9, 125.1, 78.0 ($C_{cage}$), 55.1 ($C_{cage}$). $^{11}B$ NMR (proton decoupled, 160.5 MHz): −3.80, −10.33, −13.34, −15.03. IR (KBr): 3062, 2923, 2851, 2600, 1594, 1497, 1397, 1261, 1055, 820 $cm^{-1}$. $C_{48}H_{60}B_{30}$ calcd: C 59.97, H 6.29. Found: C 59.95, H 6.30. MALDI-TOF-MS ($m/z$): calcd 961.32, found 961.71 ($M^+$, 100%). For ketone **22**, compound **12** (500 mg, 1.67 mmol) was dissolved in 20 mL of solvent (THF/toluene, 1:1). Then, 4-acetylphenylboronic acid (548 mg, 3.34 mmol), $PdCl_2(PPh_3)_2$ (47 mg, 4 mol %), and a solution of $K_2CO_3$ (691 mg, 5.01 mmol) in 3 mL of distilled water were added to it. It was refluxed at 100 °C for 24 h and then extracted with dichloromethane thrice, 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 10% ethyl acetate in hexanes as the eluent to obtain 400 mg of pure compound **22** as a colorless solid, yield 70%. Mp: 182 °C. $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 8.02 (d, 2H, $J$ = 8.36 Hz), 7.62 (d, 2H, $J$ = 8.35 Hz), 7.46 (d, 2H, $J$ = 8.50 Hz), 7.33 (d, 2H, $J$ = 8.48 Hz), 2.84 (br, s, 1H, cage-H), 2.64 (s, 3H, $CH_3$). $^{13}C$ NMR ($CDCl_3$, 125 MHz): $\delta$ 197.6, 144.4, 139.8, 136.8, 136.1, 128.9, 127.6, 127.1, 126.8, 85.8 ($C_{cage}$), 59.9 ($C_{cage}$), 26.6. $^{11}B$ NMR (proton decoupled, 160.5 MHz): −12.30, −14.88. IR (KBr): 3066, 3037, 2611, 1684, 1603, 1395, 1268, 1089, 833 $cm^{-1}$. $C_{16}H_{22}B_{10}O$ calcd: C 56.78, H 6.55. Found: C 56.75, H 6.52. MALDI-TOF-MS ($m/z$): calcd 338.45, found 338.66 ($M^+$, 100%).

*Trimer* ***23***. Ketone **22** (350 mg, 0.58 mmol) was solubilized in 20 mL of solvent (absolute ethanol/toluene 3:1). Then, $SiCl_4$ (3.6 mL, 31.02 mmol) was added to it at room temperature, and it was stirred at 50 °C temperature for 24 h. Purification of the compound with silica gel column chromatography with 2% ethyl acetate in hexanes as eluent resulted in 210 mg of pure product **23** as colorless solid. Yield: 65%. Mp: >260 °C . $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 7.85 (s, 3H), 7.78 (d, 6H, $J$ = 8.50 Hz), 7.65 (d, 6H, $J$ = 8.50 Hz), 7.48 (d, 6H, $J$ = 8.50 Hz), 7.33 (d, 6H, $J$ = 8.50 Hz), 2.84 (br, s, 3H, cage-H). $^{13}C$ NMR ($CDCl_3$, 125 MHz): $\delta$ 141.8, 140.6, 140.2, 139.2, 136.0, 127.7, 127.5, 127.4, 126.7, 126.6, 125.0, 86.1 ($C_{cage}$), 59.8 ($C_{cage}$). $^{11}B$ NMR (proton decoupled, 160.5 MHz): −12.26, −14.91. IR (KBr): 3059, 3031, 2923, 2606, 1716, 1594, 1498, 1392, 1089, 1004, 807 $cm^{-1}$. $C_{48}H_{60}B_{30}$ calcd: C 59.97, H 6.29. Found: C 59.95, H 6.28. MALDI-TOF-MS ($m/z$): calcd 961.32, found: 960.64 ($M^+$, 100%).

## ■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** $^1H$, $^{13}C$, and $^{11}B$ NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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