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PAPER

Synthesis and fluorescence emission of neutral and anionic di- and tetra-carboranyl compounds†

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A new family of photoluminescent neutral and anionic di-carboranyl and tetra-carboranyl derivatives have been synthesized and characterized. The reaction of α,α′-bis(3,5-bis(bromomethyl)phenoxy-*m*-xylene with 4 equiv. of the monolithium salt of 1-Ph-1,2-$C_2B_{10}H_{11}$ or 1-Me-1,2-$C_2B_{10}H_{11}$ gives the neutral tetracarboranyl-functionalized aryl ether derivatives *closo*-**1** and *closo*-**2**, respectively. The addition of the monolithium salt of 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ to α,α,′-dibromo-*m*-xylene or 2,6-dibromomethyl-pyridine gives the corresponding di-carboranyl derivatives *closo*-**3** and *closo*-**4**. These compounds, which contain four or two *closo* clusters, were degraded using the classical method, KOH in EtOH, affording the corresponding *nido* species, which were isolated as potassium or tetramethylammonium salts. All the compounds were characterized by IR, ^{1}H, ^{11}B and ^{13}C NMR spectroscopy, and the crystal structure of *closo*-**3** was analysed by X-ray diffraction. The carboranyl fragments are bonded through CH_2 units to different organic moieties, and their influence on the photoluminescent properties of the final molecules has been studied. All the *closo*- and *nido*-carborane derivatives exhibit a blue emission under ultraviolet excitation at room temperature in different solvents. The fluorescence properties of these *closo* and *nido*-derivatives depend on the substituent (Ph or Me) bonded to the $C_{cluster}$, the solvent polarity, and the organic unit bearing the carborane clusters (benzene or pyridine). In the case of *nido*-derivatives, an important effect of the cation is also observed.

Introduction

The twelve-vertex 1,2-*closo*-$C_2B_{10}H_{12}$ icosahedral carboranes are among the most widely studied boranes. This is mainly due to the fact that 1,2-*closo*-$C_2B_{10}H_{12}$ or their derivatives present exceptional characteristics,[1,2] such as low nucleophilicity, chemical inertness, thermal stability,[3] electron-withdrawing properties,[4] and low toxicity in biological systems.[5] These properties have stimulated the development of a wide range of potential applications, such as catalysis, materials science and even medicine.[6–8] The great potential of these systems can be increased by a carbon substitution reaction allowing the 1,2-*closo*-$C_2B_{10}H_{12}$ carborane to be grafted on macromolecules such as dendrimers,[9,10] or porphyrins,[11] among others. Also of importance, is the C–C bond in the *o*-carborane derivatives. This interesting and unusual bond displays both σ- and π-characteristics[12] that are variable depending on the substituent.[1c,13]

Recently, several papers reported the photoluminescent properties of different systems incorporating *o*-carboranes within their structures, for example: π-conjugated C_3-symmetrical structures,[14] *p*-phenylene-ethynylene-based polymers,[15] or polyfluorene conjugated polymers.[16] These studies show that the clusters interact with the aromatic π-conjugation influencing the emission properties. It appears that the introduction of *o*-carborane induces aggregation-based emission (AIE),[17] influencing the photoluminescent properties of polyfluorene, whereas the variable C–C bond acts as a quencher to fluorescence from phenylene-ethylene segments. Nevertheless, the presence of *o*-carborane clusters in π-conjugated C_3-symmetric systems separarted by a methylene moiety prevents π–π stacking and enhances fluorescence intensity.[14b]

In a previous work,[18] we reported high-boron content neutral and anionic tetracarboranyl-functionalized aryl-ether derivatives that exhibited fluorescence emission in different solvents at room temperature. We proposed that specific interactions between the organic substituents and the cluster induce changes in the

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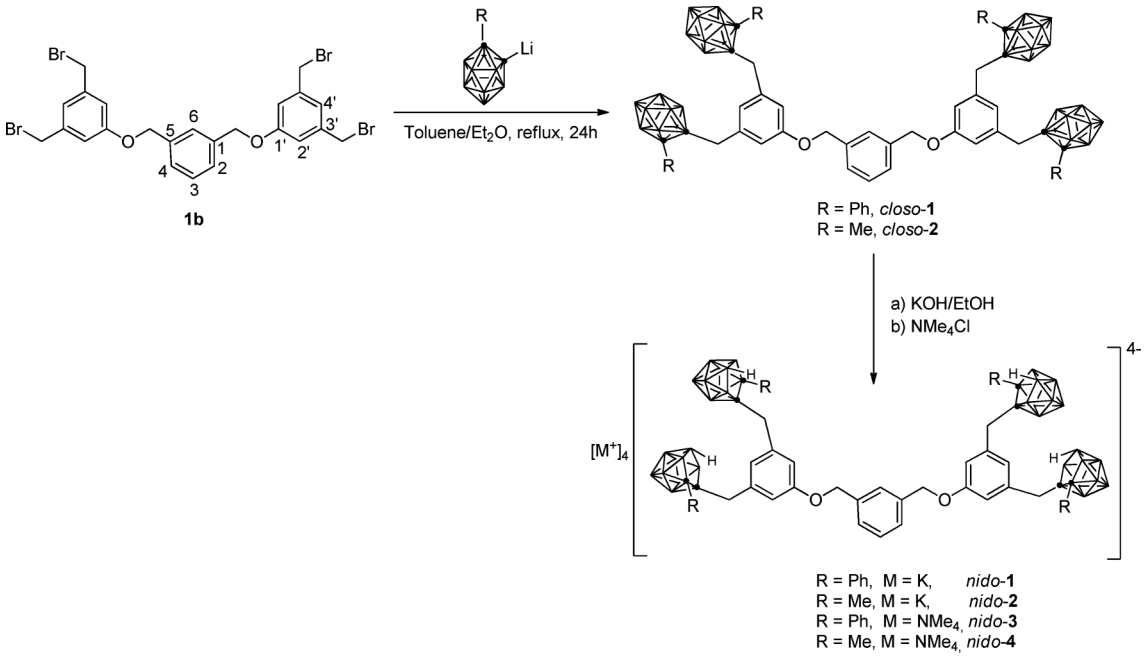


Scheme 1 Synthesis of neutral and anionic tetra-carboranyl compounds.

electronic structure of the carborane cage. We also pointed out that solvent polarity influences the emission properties. Thus, pursuing our work dealing with the preparation, functionalization and photoluminescent properties of carboranyl-containing derivatives, we report herein the preparation of a new set of compounds, in which *o*-carboranyl units have been bonded to different cores. As a first step we have investigated the influence of a *meta*-substitution in the central benzene of the tetracarboranyl-containing aryl-ether molecule instead of a *para*-substitution. We have also synthesized smaller compounds consisting of two carborane clusters bonded to benzene and pyridine rings in *meta* positions. A comparative study of the photoluminescent properties for all compounds has been carried out in different solvents at room temperature. The crystal structure of one of these compounds has been analysed by X-ray diffraction.

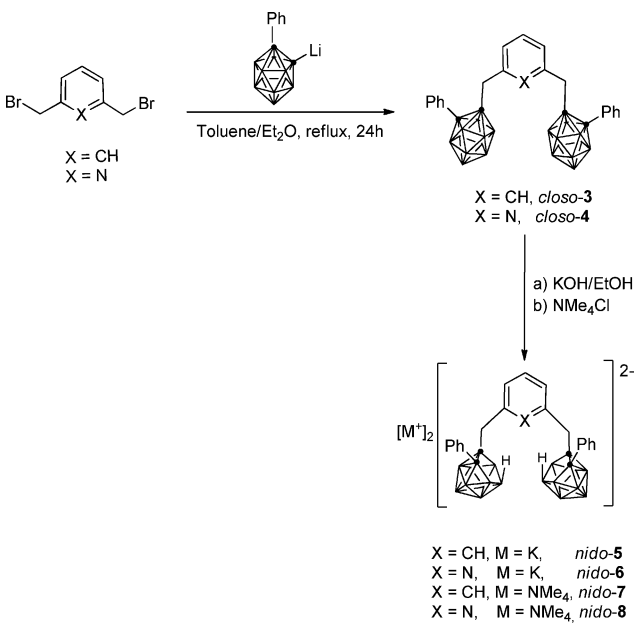
Results and discussion

Synthesis of starting compounds

α,α-Bis(3,5-bis(bromomethyl)phenoxy-*m*-xylene (**1b**) was prepared from tetra-alcohol α,α-bis(3,5-bis(hydroxymethyl)phenoxy-*m*-xylene (**1a**)[19] by treatment with CBr_4 and PPh_3 in THF at room temperature for 16 h, following similar conditions to those previously reported by us.[18] In addition, 2,6-bis(bromomethyl)pyridine (**3**) was prepared by reaction of 2 equiv. of PBr_3 on the diol 2,6-dihydroxymethyl-pyridine in $CHCl_3$ at 40 °C for 3 h, according to a published procedure.[20]

Synthesis of neutral and anionic di- and tetra-carboranyl compounds

Grafting of *closo*-carborane units to aryl-ether derivatives was performed following a procedure previously described by our group.[18] Briefly, after adding 4 equiv. of the freshly prepared monolithium salts of 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ or 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$ on compound **1b** in THF, the mixture was refluxed 16 h to 24 h to afford *closo*-**1** or *closo*-**2**, in 61 and 70% yields, respectively (Scheme 1). In a similar way, by addition of the monolithium salt of 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ in THF to α,α,′-dibromo-*m*-xylene (**2**) or 2,6-bis(bromomethyl)pyridine (**3**), and after refluxing 16 h, the carboranyl derivatives *closo*-**3** or *closo*-**4** were obtained in 75% and 78% yields, respectively (Scheme 2). Compound *closo*-**3** was crystallized from a solution of acetone to give monocrystals suitable for X-ray diffraction analysis. Subsequently, partial degradation of *closo*-**1** and *closo*-**2** was achieved using an excess of KOH in ethanol at reflux for 20 h; the



Scheme 2 Synthesis of neutral and anionic di-carboranyl compounds.

Table 1 Supramolecular interactions between neighboring carboranes in the crystal packing of compound *closo*-**3**

	d H–H (Å)	*d* C–B (Å)	∠ CH···H (°)	∠ BH···H (°)
C(8)H(8)···H(5A)B(5)	2.327	3.968	147.51	131.78
C(8)H(8)···H(15A)B(15)	2.304	3.946	140.64	139.12
C(3)H(3B)···H(10)B(10)	2.538	3.756	111.79	124.38
C(10)H(10)···H(20A)B(20)	2.413	3.667	122.45	114.42

obtained potassium salts were isolated affording *nido*-**1** and *nido*-**2**, respectively. Finally, the anions were isolated by precipitation with [Me_4N]Cl, to give the tetramethylammonium salts *nido*-**3** and *nido*-**4** (Scheme 1). Partial degradation of *closo*-**3** and *closo*-**4** gave the respective *nido*-**5** and *nido*-**6** as the potassium salts that after precipitation with [Me_4N]Cl led to *nido*-**7** and *nido*-**8** (Scheme 2). Although the potassium salts were difficult to isolate due to their hygroscopic character, we were able to characterize them by NMR spectroscopy. The potassium salts are soluble in water and polar solvents such as EtOH or DMSO.

Characterization of di- and tetra-carboranyl compounds

All compounds were characterized by means of IR, ^{1}H, ^{11}B and ^{13}C NMR, and UV-vis spectroscopies. The IR spectra of *closo*-derivatives exhibit a strong absorption at 2580 cm^{-1} assigned to the B–H stretching vibration, while for *nido* compounds this band appears around 2516 cm^{-1} whatever the organic moieties, giving a first evidence of the effective degradation.

The ^{1}H NMR spectrum of starting **1b** shows four resonances at 7.53, 7.47, 7.05 and 6.97 ppm assigned to the aromatic protons, whereas two singlets at 5.11 and 4.45 ppm are observed in the aliphatic region attributed to the benzyl ether and benzyl bromide protons, respectively. Compound **2** exhibits three aromatic signals at 7.39, 7.31 and 7.29 ppm in the ^{1}H NMR spectrum and only one for the benzyl bromide protons at 4.44 ppm, whereas **3** presents only two resonances for the pyridine unit at 7.72 and 7.39 ppm, and the CH_2 protons appear as a singlet at 4.56 ppm. In all cases, grafting of carborane units was established by a clear shift of benzyl bromide protons in the starting compound to lower frequencies: 2.97 ppm for *closo*-**1**, 3.69 ppm for *closo*-**2**, 3.20 ppm for *closo*-**4** and 3.04 for *closo*-**3**. Compounds containing the 1-Ph-1,2-$C_2B_{10}H_{10}$ exhibit additional signals in the 6 to 7 ppm range relative to the aromatic protons. For *closo*-**2** a singlet centred at 2.30 ppm integrating for 12H evidences the grafting of 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$ on the organic core. The presence of the clusters in the molecules was also confirmed by ^{13}C{^{1}H} NMR spectra that show two resonances, between 84 and 82 ppm, assigned to the $C_{cluster}$ for phenyl-*o*-carborane derivatives. A shift of those signals to higher fields, 78.52 and 76.17 ppm, was observed for *closo*-**2**. After partial degradation, ^{1}H NMR spectra of all of the *nido* compounds exhibit a broad singlet, between –1.92 and –2.62 ppm attributed to the B–H–B bridge proton. Compounds *nido*-**2** and *nido*-**4** exhibited two very close resonances in the 1.34 and 1.32 ppm region, integrating 6H each that were attributed to the methyl protons of the cluster, indicating a loss of symmetry. Other evidence consistent with this symmetry loss is observed when resonances assigned to H-4/H-2 protons appear at 6.79 and 6.85 ppm for *nido*-**2**, and at 6.74 and 6.80 ppm for *nido*-**4**. In the case of the *nido* compounds bearing phenyl-*o*-carborane units, very interesting features were observed in the 2.7 to 2.5 ppm region of their ^{1}H NMR spectra that are assigned to the methylene protons bonded to the clusters. The loss of symmetry was clearly evidenced by the observation of AB systems for the diastereotopic benzyl protons. The coupling constant values varying from 14.9 to 16.8 Hz are consistent with a geminal position. All of these observations were confirmed by inspection of the ^{13}C NMR spectra for *nido* species that show a greater complexity of the system, and for that reason no attempts to assign the different signals have been made. However, it is relevant to note that in all cases two different resonances attributed to the benzylic protons bonded to the cluster were observed around 42 ppm. The loss of symmetry can be easily explained by the two possibilities of partial degradation in $C_2B_{10}H_{12}$ derivatives, either in B(3) or B(6). When the *o*-carboranyl fragment is singly bonded to a platform as is the current case, the partial degradation leads to two enantiomers.

The ^{11}B NMR spectrum of *closo*-**2** shows three broad resonances centred at –3.55, –5.15 and –9.27 ppm, with the ratio 1 : 1 : 8. *closo*-**1**, *closo*-**3** and *closo*-**4** showed two signals around –2 and –9 ppm with the ratio 2 : 8. A completely different spectrum was obtained for *nido* derivatives that exhibit four to seven resonances, in the range –6.05 to –35.60 ppm, corroborating the decapitation of the carborane cage.

The Ortep plot of *closo*-**3** with the labelling system used is presented in Fig. 1. *closo*-**3** has a pseudo-twofold axis through C5–C8. The C1–C2 and C11–C12 bond lengths are 1.707(7) and 1.706(7) Å, respectively. All other bonding parameters are normal. The crystal packing is dominated by very weak BH···HB and BH···HC contacts. The supramolecular structure is defined by two types of intermolecular interactions,[21] CH···HB between two parallel displaced columns (see Fig. 2), which are summarized in Table 1. The methylene groups (atoms C3 and C10) interact with two different BH carborane fragments within the same column. Interactions between columns concurrently occur among the aromatic proton H8 and the H15A and H5A hydrides coming from two different carboranes of two different molecules, leading to void channels (Fig. 2b). In the unit cell of *closo*-**3** there are 8 voids each having a volume of 19 Å^3. The amount of the voids is only about 2.5% of the total volume of the unit cell (Fig. 2b). Fig. 3 shows a perspective view of the packing forms by intermolecular interactions between adjacent molecules from groups of columns in a zig-zag array.

Photophysical properties of di- and tetra-carboranyl compounds

Emission results at room temperature show that phenyl-*o*-carborane derivatives exhibit maximum emission intensities (λ_{em}) between 369 and 371 nm reasonably independent of the solvent. Conversely, compounds containing methyl-*o*-carborane exhibit a λ_{em} in a wide range, 333–363 nm, depending on the solvent

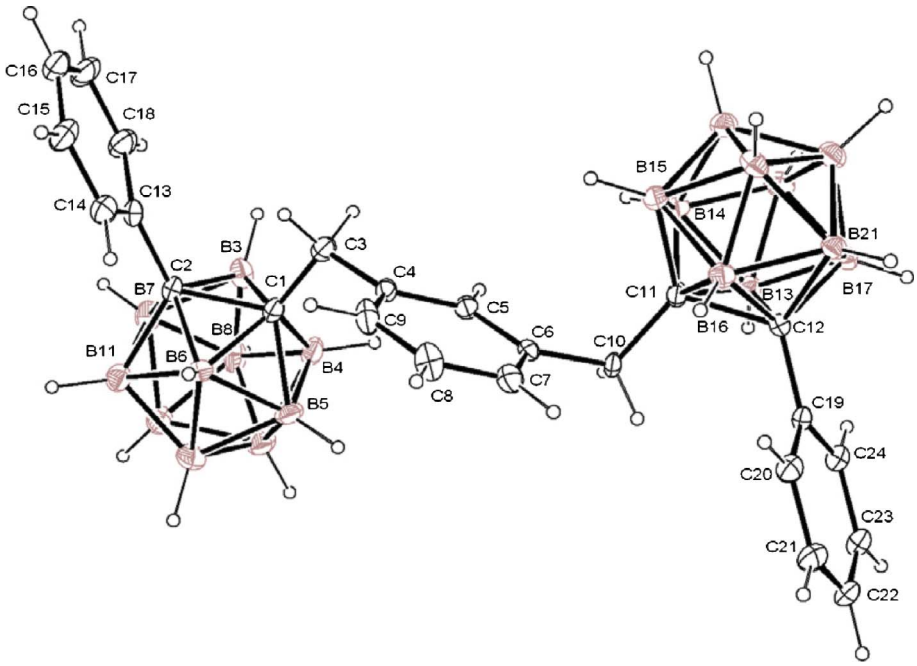


Fig. 1 Ortep plot of solid state structure of *closo*-**3**. Thermal ellipsoids are drawn at 20% level.

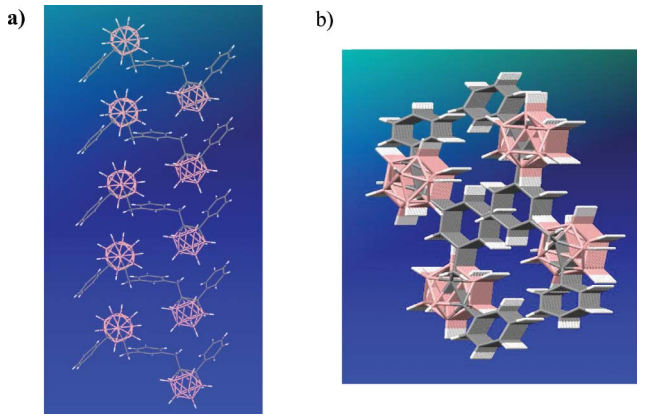


Fig. 2 a) A perspective of the packing in the crystal lattice of compound *closo*-**3**, through the crystallographic *ab* plane (a) and *ac* plane (b).

(Table 2). It is important to emphasize that isolated initial carboranyl precursors 1-Ph-1,2-$C_2B_{10}H_{11}$ and 1-Me-1,2-$C_2B_{10}H_{11}$ exhibited no emission at r.t. If λ_{em} of *closo*-**1** is compared with λ_{em} of *closo*-**2**, a bathochromic shift of 30 nm is observed in THF

Table 2 Fluorescence emission data at 5×10^{-4} M, in solution at room temperature

	λ_{em} (nm)	
Compound	THF	Other solvent
closo-**1**	369[a]	371[a] (Toluene)
closo-**2**	333[a]	363[a] (Toluene)
nido-**1**	370[b]	373[a] (H_2O)
nido-**2**	339[b]	362[b] (H_2O)
nido-**3**	369[a]	371[a] (DMSO)
nido-**4**	338[a]	366[b] (DMSO)

[a] After excitation at 310 nm. [b] After excitation at 300 nm.

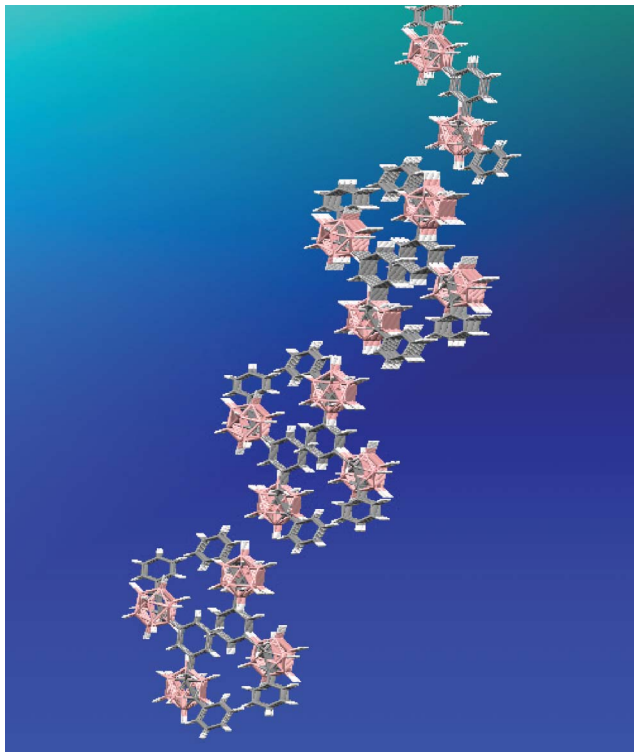


Fig. 3 A perspective of the crystal packing of *closo*-**3** highlighting the zig-zag array.

and around 10 nm in toluene (Fig. 4). The significant fluorescence λ_{em} solvent dependence of *closo*-**2** and the solvent independence of *closo*-**1** can be attributed to an interaction of C–H from the methyl group with the solvent, induced by the strong electron-withdrawing character of the *o*-carboranyl moiety.

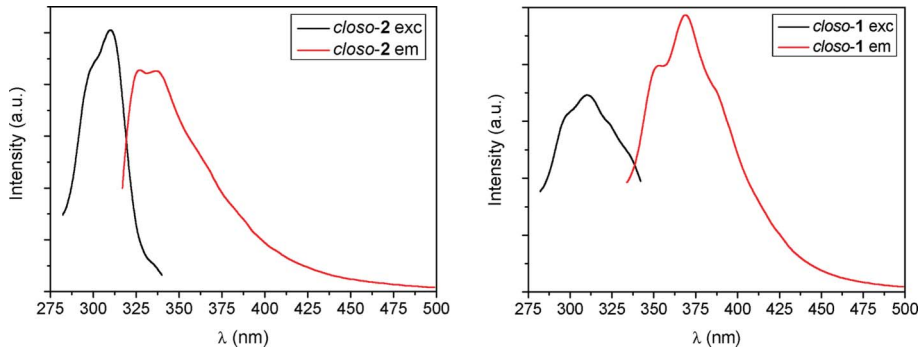


Fig. 4 Fluorescence emission for *closo*-**2** (left) and *closo*-**1** (right) in THF.

After partial degradation of the carborane cages in *closo*-**1** and *closo*-**2**, the emission properties of the corresponding *nido* compounds are in the range 338–373 nm, depending on the solvent (Table 2). Both *nido*-**1** and *nido*-**3** show a weak red shift, 2–3 nm, comparing their emissions in THF and other solvents. The same behaviour is observed with *nido*-**2** and *nido*-**4** with a larger shift, 23 nm and 28 nm, respectively (Table 2). The difference in the Stoke's shift for the anionic compounds in different solvents indicates that interactions between the chromophore and the medium on the excited states take place. The charge of the carboranyl species has an influence on the polarity of the chromophore leading to a higher sensitivity of the excited state to solvent effects. Increasing the solvent polarity produces a correspondingly larger reduction in the energy level of the excited state, while decreasing the solvent polarity reduces the solvent effect on the excited state energy level.[22]

In fact, the behaviour of these *meta*-substituted aryl-ether derivatives carrying either methyl or phenyl-*o*-carboranes units is similar to that found previously for *para*-substituted aryl-ether derivatives.[18] These results corroborate the low influence of the organic core configuration on the emission properties of the final carboranyl-containing compounds.

This minor influence of the aryl-ether substitution on the core indicates that the photoluminescence is related with the peripheral part of the molecule bearing the carboranyl fragments bonded to one benzene ring through a CH_2 bridge. This prompted us to synthesize smaller dicarboranyl-containing molecules similar to the existing peripheral fragments in *closo*-**1** and *closo*-**2**, and *nido*-**1** to *nido*-**4**. In this way, *closo*-**3** was synthesized and its emission

Table 3 Fluorescence emission data at 5×10^{-4} M, in solution at room temperature

	$\lambda_{em\ (nm)}$		Stokes shift (nm)	
Compound	THF	Other solvent	THF	Other solvent
closo-**3**	371[a]	370[a] (Toluene), 373[a] ($CHCl_3$)	61	60 (toluene)
closo-**4**	343[a]	372[a] (Toluene), 375[a] ($CHCl_3$)	33	62 (toluene)
nido-**5**	348[b]	415 (H_2O)[c]	48	32 (H_2O)
nido-**6**	353[a]	482 (H_2O)[d]	43	89 (H_2O)
nido-**7**	341[b]	342[a] (DMSO)	41	32 (DMSO)
nido-**8**	340[a]	365[b] (DMSO)	30	65 (DMSO)

[a] After excitation at 310 nm. [b] After excitation at 300 nm. [c] After excitation at 383 nm. [d] After excitation at 393 nm.

bands compared to those of *closo*-**1** (Table 3). As expected, and according to the results obtained for *closo*-**1**, both display very similar λ_{em} whatever the solvent used, with a maximum of emission around 370 nm (Fig. 5). However, the fluorescence emission intensity is dependent on the solvent reaching its maximum in toluene, with lower intensities in $CHCl_3$ and THF, which is similar to the results described in a previous work.[18] If the intensities are compared with a common solvent, the tetracarboranyl-containing *closo*-**1** shows a higher intensity than the dicarboranyl-containing *closo*-**3**, probably due to the fact that the former carries twice the numbers of luminescent units.

To complete this study *closo*-**4** has been synthesized. It shows a similar structure to *closo*-**3**, however in this case the benzene ring has been replaced by a pyridine ring carrying two carborane units. We expected that the existence of one N atom in the aromatic ring

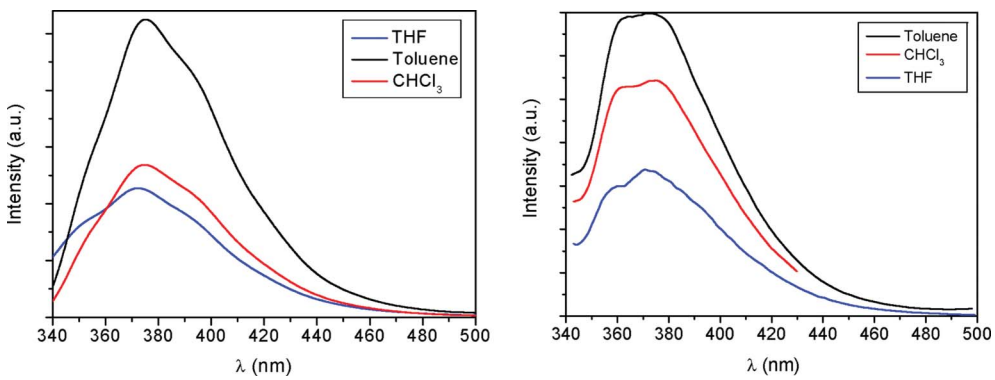


Fig. 5 Emission spectra of *closo*-**1** (left) and *closo*-**3** (right) in several solvents.

could induce some differences in the photoluminescent properties, as weak hydrogen bonding interactions with the solvent could be produced.

Certainly the behaviour of *closo*-**4** is clearly affected by the solvent: a) a stronger fluorescence intensity combined with a lower λ_{em} was observed in THF as compared to toluene or $CHCl_3$ (Table 3, Fig. 6); b) it was also observed a 42 nm shift from 343 nm in THF to 385 nm in acetone (Fig. 6). The smaller Stokes shift observed for *closo*-**4** in THF compared with *closo*-**3** (Table 3) along with the highest emission intensity (Fig. 6) could be due to interactions between the pyridine ring and THF. Indeed, since *closo*-**3** does not exhibit such properties, it can be interpreted that the pyridine acts as a stronger dipole than the benzene ring in *closo*-**3**, leading to a different behaviour depending on the solvent polarity.[22]

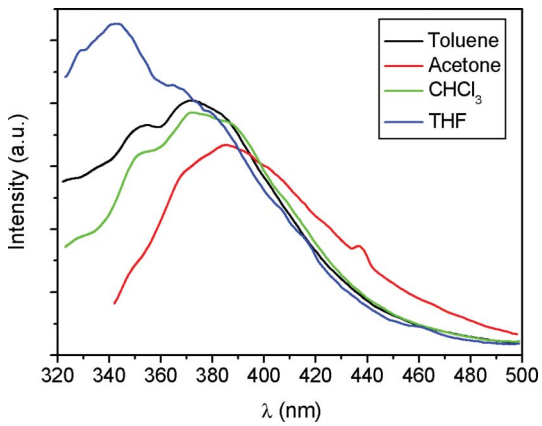


Fig. 6 Fluorescence emission spectra of *closo*-**4** in different solvents.

As described earlier, the carborane cages in *closo*-**3** and *closo*-**4** can be partially degraded leading to the corresponding *nido* species. The benzene derivatives *nido*-**5** and *nido*-**7** show the same behaviour in THF as the pyridine derivatives *nido*-**6** and *nido*-**8**. The *nido*-**5** exhibits a maximum emission at 348 nm that shifts to 341 nm for *nido*-**7**, whereas their Stokes shifts follow the same trend, from 48 to 41 nm (Table 3). Concerning the pyridine species, *nido*-**6** and *nido*-**8**, a 13 nm decrease of λ_{max} and the Stokes shift is observed (Table 3). For these compounds the only difference is the cation (K^+ or $[NMe_4]^+$) associated with the *nido* cage. The emission properties in THF of *nido* derivatives with the same cation, that is *nido*-**5** and *nido*-**6** or *nido*-**7** and *nido*-**8**, are roughly the same with a band in the 348–353 nm range and 340–341 nm, respectively (Table 3). In these examples, the larger cation seems to lead to a lower λ_{max} and a lower Stokes shift. These results indicate a lower influence of the aromatic units (benzene or pyridine) when carrying *nido* cages and a significant effect of the cation on the fluorescence in THF. Nevertheless, such behaviour is not observed in the case of more complex structures such as *nido*-**1** and *nido*-**3** or *nido*-**2** and *nido*-**4**, because the maximum of emission remains the same in THF independent of the cation (Table 3). In these, the participation of the ether units of the aryl-ether core in weak interactions with the cations could be the reason for this observation. These interactions would compete with the *nido*-carborane/cation interaction, thus masking the cation influenced fluorescence observed for *nido*-**5** to *nido*-**8**.

When measurements are performed in H_2O, the results obtained with *nido*-**5** and *nido*-**6** are very different from those observed in THF. The excitation wavelengths are red shifted from 300 and 310 nm in THF to 383 and 393 nm in H_2O (Table 3), and the emission bands are located in the 415–482 range (Fig. 7). This red shift of the excitation and emission bands is in agreement with a bathochromic effect due to the higher polarity of H_2O compared to THF.

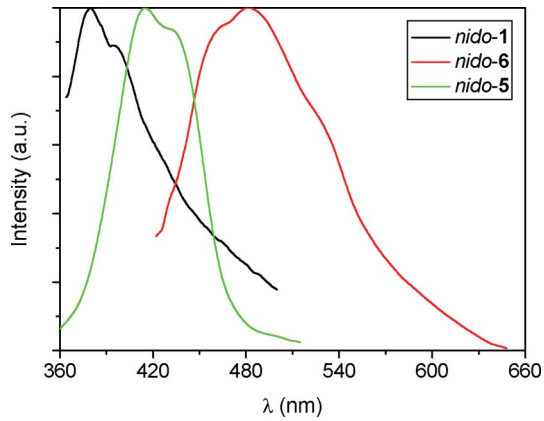


Fig. 7 Normalized fluorescence emission spectra of *nido*-**1** (exc 300 nm), *nido*-**5** (exc 383 nm) and *nido*-**6** (exc 393 nm) in H_2O.

Finally *nido*-**5** exhibits a lower Stokes shift in H_2O (30 nm) than in THF (48 nm), whereas *nido*-**6** behaves differently with a Stokes shift of 89 nm (Table 3). This difference is also observed between *nido*-**7** and *nido*-**8** in DMSO. In both cases the highest Stokes shift is observed with the pyridine derivatives, indicating that the dipole moment of these molecules are higher in the excited state than in the ground state, providing an increase of the Stokes shifts with the solvent polarity.[22]

Conclusions

A new family of neutral and anionic di-carboranyl and tetra-carboranyl derivatives have been synthesized and characterized. The carboranyl fragments are bonded through CH_2 units on different organic moieties, and their influence on the photoluminescent properties of the final molecules has been studied. All the *closo*- and *nido*-carborane derivatives exhibit a blue emission under ultraviolet excitation at room temperature in different solvents. The fluorescence studies in these *closo*-derivatives indicate that the maximum of emissions depend on several factors such as: the substituent (Ph or Me) bonded to the $C_{cluster}$, the solvent polarity, and the organic unit bearing the carborane clusters (benzene or pyridine). In the case of *nido*-derivatives, an important effect of the cation is also observed. Nevertheless, few differences on the maxima emission bands are observed between tetra-carboranyl *closo* and *nido*-species, whereas a major influence of the cluster nature is observed for di-carboranyl compounds. This last effect is attributed to the participation of the ether units of the aryl-ether core in weak interactions with the cations. It is important to notice that the common fragment in all these compounds is the CH_2 bridge between the carborane cage and the aromatic ring, which seems to prevent π–π stacking. In our opinion this is the key

of the photoluminescence properties especially since compounds without this moiety do not display such a feature.

Experimental

Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. The ^{1}H NMR (300.13 MHz), $^{11}B\{^{1}H\}$ NMR (96.29 MHz) and $^{13}C\{^{1}H\}$ NMR (75.47 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. All NMR spectra were recorded in $CDCl_3$ or CD_3COCD_3 solutions at 25 °C. Chemical shift values for $^{11}B\{^{1}H\}$ NMR spectra were referenced to external $BF_3{\cdot}OEt_2$, and those for ^{1}H and $^{13}C\{^{1}H\}$ NMR were referenced to $SiMe_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are reported in Hertz. Fluorescence spectra were measured on a Cary Eclipse Fluorescence Spectrophotometer, using solutions of compounds at 5×10^{-4} mol L^{-1}.

All reactions were performed under an atmosphere of dinitrogen employing standard Schlenk techniques. THF, Et_2O and toluene were purchased from Merck and distilled from sodium benzophenone prior to use, and CH_3CN was received from J. T. Baker Co. Compounds 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ and 1-Me-1,2-*closo*-$C_2B_{10}H_{11}$ were supplied by Katchem Ltd. (Prague) and used as received. Compounds **1a**[19] and 2,6-bis(bromomethyl)pyridine (**3**)[20] were synthesized according to the literature. *n*-BuLi solution (1.6 M in hexane) was purchased from Lancaster or Aldrich. Starting materials: α,α,′-dibromo-*m*-xylene (**2**); 3,5-dihydroxybenzoic acid; 1,3-dihydroxymethyl-pyridine, triphenylphosphine; carbon tetrabromide; potassium carbonate; lithium hydride and phosphorous tetrabromide were commercially available from Aldrich and used as received.

Synthesis of α,α′-bis[3,5-bis(bromomethyl)phenoxy]-*m*-xylene (1b)

To a solution of **1a** (3.435 g, 8.4 mmol) and CBr_4(16.71 g, 50.2 mmol) in dry THF was added PPh_3 (22.55 g, 86.05 mmol) in two portions. The reaction mixture was stirred at room temperature under N_2 for 16 h. The pH was adjusted to 7 with Na_2CO_3 (20 mL), and brine (80 mL) was added. The aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL). The organic phases were collected and concentrated under vacuum. The residue was passed through a short column of silica gel, washed with hexane and eluted with a 85 : 15 hexane : ethyl acetate mixture to give **1b** as a white powder (3.023 g, 4.56 mmol) yield 55.0%, mp 139–143 °C. IR (KBr, cm^{-1}): 3445, 2883, 1722, 1594, 1445, 1334, 1300, 1211, 1178, 1040, 697, 551. MS, *m*/*z* (%) [M^+, 662 (1)]: 583 (3), 385 (50), 383 (100), 381 (49), 303 (15), 223 (15), 183 (30), 104 (27). ^{1}H NMR (270 MHz, $CDCl_3$): 7.53 (1H, H-6, s), 7.47 (3H, H-2,H-3, H-4, s), 7.05 (2H, H-4′, s), 6.97 (4H, H-2′, s), 5.11 (4H, CH_2O, s), 4.45 (8H, CH_2Br, s). ^{13}C NMR (67.94 MHz, $CDCl_3$): 159.3 (C-1′), 139.6 (C-1), 137.1 (C-3′), 129.2 (C-3), 127.5 (C-2), 126.8 (C-6), 122.4 (C-4′), 115.7 (C-2′), 70.1 (CH_2O), 33.0 (CH_2Br).

Synthesis of *closo*-1

To a solution of phenyl-*o*-carborane (294 mg, 1.33 mmol) in 3 mL of dry diethyl ether at 0 °C, was added a 1.6 M solution of *n*-BuLi in hexane (0.98 mL, 1.46 mmol). When addition was completed, the mixture was stirred 45 min at room temperature. The light yellow solution was cooled to 0 °C and a suspension of **1b** (200 mg, 0.30 mmol) in a dry toluene/diethyl ether (2 : 1) mixture (6 mL) was added. After refluxing for 24 h, the orange mixture was quenched with 15 mL of water and transferred to a separatory funnel. The layers were separated and the aqueous layer was extracted with additional diethyl ether (2 × 6 mL). The combined filtrates were dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give a yellow residue. The solid obtained was taken up in hexane, after filtration the suspension gave 224 mg (0.18 mmol, yield 61%) of a yellow solid. ^{1}H NMR ($(CD_3)_2CO$): 7.67 (d, 8H, $^{3}J_{ortho}$ = 7.32 Hz), 7.44 (m, 16H), 6.33 (s, 4H), 5.88 (s, 2H), 4.98 (s, 4H), 2.97 (s, 8H). ^{13}C NMR ($(CD_3)_2CO$): 158.44, 137.41, 136.84, 131.51, 131.22, 130.35, 129.33, 128.77, 126.95, 126.37, 124.36, 116.20, 84.00, 82.40, 69.51, 40.31. ^{11}B NMR ($(CD_3)_2CO$): −1.51 (s, 2B), −8.09 (s, 8B). IR (KBr, cm^{-1}): 3062 ν(C–H_{aryl}), 2931 ν(C–H_{alky}), 2584 ν(B–H), 1596, 1072. Elemental Analysis Calcd (%) for $C_{56}H_{82}B_{40}O_2$: C 55.10, H 6.72; Found: C 55.53; H 6.86.

Synthesis of *closo*-2

To a solution of methyl-*o*-carborane (300 mg, 1.89 mmol) in 3 mL of dry diethyl ether at 0 °C, was added a 1.6 M solution of n-BuLi in hexane (1.35 mL, 2.08 mmol). When addition was completed, the mixture was stirred 45 min at room temperature. The light yellow solution was cooled to 0 °C and a suspension of **1b** (299 mg, 0.45 mmol) in a dry toluene/diethyl ether (2 : 1) mixture (9 mL) was added. After refluxing for 16 h, the yellow mixture was quenched with 15 mL of water and transferred to a separatory funnel. The layers were separated and the aqueous layer was extracted with additional diethyl ether (2 × 10 mL). The combined filtrates were dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give a yellow residue. The solid obtained was taken up in hexane, after filtration the white suspension gave 295 mg (0.30 mmol, yield 70%) of a light yellow solid. ^{1}H NMR ($(CD_3)_2CO$): 7.60 (s, 1H), 7.46 (s, 3H); 6.98 (s, 4H), 6.90 (s, 2H), 5.22 (s, 4H), 3.69 (s, 8H), 2.30 (s, 12H). ^{13}C NMR ($(CD_3)_2CO$): 158.77, 137.45, 137.38, 128.74, 127.07, 126.64, 125.05, 116.68, 78.52, 76.17, 69.67, 40.26, 22.99. ^{11}B NMR ($(CD_3)_2CO$): −3.55 (s, 1B), −5.15 (s, 1B), −9.27 (s, 8B). IR (KBr, cm^{-1}): 2943 ν(C–H_{alkyl}), 2584 ν(B–H), 1596, 1054. Elemental Analysis Calcd (%) for $C_{36}H_{74}B_{40}O_2$: C 44.51, H 7.62; Found: C 45.02; H 7.42.

Synthesis of *closo*-3

To a solution of phenyl-*o*-carborane (369 mg, 1.66 mmol) in 4 mL of dry THF at 0 °C, was added a 1.6 M solution of n-BuLi in hexane (1.33 mL, 2.00 mmol). When addition was completed, the mixture was stirred 45 min at room temperature. The light red solution was cooled to 0 °C and a solution of α,α,′-dibromo-*m*-xylene (**2**) (200 mg, 0.75 mmol) in dry THF (4 mL) was added. After refluxing for 18 h, THF was distilled off to give a dark orange residue. The solid was quenched with 30 mL of water and 15 mL of ether were added, the resulting mixture was transferred to a separatory funnel. The layers were separated and the aqueous layer was extracted with additional diethyl ether (2 × 6 mL). The combined filtrates were dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give a yellow residue. Recrystallization in acetone gave *closo*-**3** as white crystals (316 mg, 0.58 mmol, yield 75%). ^{1}H NMR ($CDCl_3$): 7.71 (d, 4H, $^{3}J_{ortho}$ 7.3 Hz), 7.49 (m,

6H), 7.12 (dd, 1H, $^{3}J_{ortho}$ 7.7 Hz), 6.71 (d, 2H, $^{3}J_{ortho}$ 7.7 Hz), 6.29 (s, 1H), 3.04 (s, 4H). ^{13}C NMR ($CDCl_3$): 136.32, 132.58, 132.44, 131.88, 131.72, 130.47, 130.03, 129.36, 84.53, 82.64, 41.78. ^{11}B NMR ($CDCl_3$): –2.66 (s, 2B), –9.29 (s, 8B). IR (KBr, cm^{-1}): 3060 ν(C–H_{aryl}), 2931 ν(C–H_{alky}), 2580 ν(B–H), 1596, 1072. Elemental Analysis Calcd (%) for $C_{24}H_{38}B_{20}$: C 53.06; H 7.00; Found: C 53.23; H 7.18.

Synthesis of *closo*-4

Using the same procedure as described for *closo*-**3**, using phenyl-*o*-carborane (368, 1.66 mmol), *n*-Buli (1.26 mL, 2.00 mmol) and **3** (200 mg, 0.75 mmol), was obtained *closo*-**4** as a light yellow solid (320 mg, 0.58 mmol, yield 78%). ^{1}H NMR ($CDCl_3$): 7.76 (d, 4H, $^{3}J_{ortho}$ 7.3 Hz), 7.46 (m, 7H), 6.75 (d, 2H, $^{3}J_{ortho}$ 7.7 Hz), 3.20 (s, 4H). ^{13}C NMR ($CDCl_3$): 155.86, 137.75, 132.49, 131.81, 131.72, 129.96, 124.45, 84.68, 81.47, 43.74. ^{11}B NMR ($CDCl_3$): –3.65 (s, 2B), –10.09 (s, 8B). IR (KBr, cm^{-1}): 3060 ν(C–H_{aryl}), 2931 ν(C–H_{alky}), 2581ν(B–H), 1593, 1065. Elemental Analysis Calcd (%) for $C_{23}H_{37}B_{20}N$: C 50.76; H 6.80; Found: C 51.02; H 6.92.

Synthesis of *nido*-1

closo-**1** (100 mg, 0.082 mmol) was added to a solution of KOH (40 mg, 0.656 mmol) in 4 mL of deoxygenated EtOH. The white suspension was stirred for 1 h at room temperature and refluxed 20 h. After cooling the mixture, the excess of KOH was precipitated as potassium carbonate by saturating the solution with a stream of CO_2(g). After filtration the solution was evaporated to give a white residue. The solid was taken up in THF, and the suspension was stirred at room temperature for a few minutes. After filtration, the THF solution was evaporated to dryness to give *nido*-**1** as a white solid. Yield: 95 mg, 87%. ^{1}H NMR ($(CD_3)_2CO$): 7.47 (s, 1H), 7.40 (m, 3H), 7.10 (m, 8H), 7.01 (m, 12H), 6.20 (s, 1H), 6.17 (s, 1H), 5.87 (s, 4H), 3.63 (t, 16H, THF), 4.89 (s, 4H), 2.61 (d, 2H, $^{2}J_{gem}$ 16.6 Hz), 2.57 (d, 2H, $^{2}J_{gem}$ 16.6 Hz), 2.52 (d, 2H, $^{2}J_{gem}$ 16.6 Hz), 2.47 (d, 2H, $^{2}J_{gem}$ 16.6 Hz), 1.79 (t, 16H, THF), –2.26 (s, 4H). ^{13}C NMR ($(CD_3)_2CO$): 157.16, 141.93, 138.08, 132.22, 129.04, 127.84, 127.27, 127.05, 126.57, 125.96, 124.95, 123.74, 112.98, 69.24, 68.07, 67.29, 63.14, 42.75, 42.24, 26.15. ^{11}B NMR ($(CD_3)_2CO$): –6.47 (s, 2B), –14.35 (s, 5B), –30.36 (s, 1B), –33.41 (s, 1B). IR (KBr, cm^{-1}): 3031 ν(C–H_{aryl}), 2931 ν(C–H_{alkyl}), 2522 ν(B–H), 1658, 1407, 1006. Elemental Analysis Calcd (%) for $C_{56}H_{82}B_{36}K_4O_2{\cdot}4(C_4H_8O)$: C 53.34; H 7.03. Found: C 54.29; H 6.59.

Synthesis of *nido*-3

Elaboration of *nido*-**3** followed the same experimental route as *nido*-**1**, until the mixture was cooled to r.t. EtOH was evaporated to give a white residue which was dissolved in water. Addition of an excess of Me_4NCl in water solution gave a precipitate. After filtration the solid was dried *in vacuo* to give *nido*-**3** as a white powder. Yield: 113 mg, 94%. ^{1}H NMR ($(CD_3)_2CO$): 7.65 (s, 1H), 7.51 (m, 3H), 7.25 (d, 8H, $^{3}J_{ortho}$ 7.5 Hz), 7.01 (m, 12H), 6.52 (s, 4H), 5.93 (s, 1H), 5.89 (s, 1H), 5.04 (s, 4H), 3.34 (s, 48 H), 2.61 (d, 2H, $^{2}J_{gem}$ 14.9 Hz), 2.57 (d, 2H, $^{2}J_{gem}$ 14.9 Hz), 2.52 (d, 2H, $^{2}J_{gem}$ 14.9 Hz), 2.47 (d, 2H, $^{2}J_{gem}$ 14.9 Hz), –2.13 (s, 4H). ^{13}C NMR ($(CD_3)_2CO$): 159.36, 143.13, 139.01, 133.52, 128.10, 127.74, 127.27, 127.05, 126.57, 125.96, 124.85, 124.11, 113.05, 68.14, 66.29, 62.24, 55.20, 42.83, 41.97. ^{11}B NMR ($(CD_3)_2CO$): –6.05 (s, 2B), –14.55 (s, 5B), –31.76 (s, 1B), –34.21 (s, 1B). IR (KBr, cm^{-1}): 3031 ν(C–H_{aryl}), 2920 ν(C–H_{alky}), 2518 ν(B–H), 1591, 1483, 1029. Elemental Analysis Calcd (%) for $C_{72}H_{130}B_{36}N_4O_2$: C 58.65 H 8.82; N 3.80. Found: C, 58.11; H, 8.82; N, 3.54.

Synthesis of *nido*-2

The degradation procedure was the same as for *nido*-**1**, using *closo*-**2** (100 mg, 0.10 mmol) and KOH (46 mg 0.82 mmol). Compound *nido*-**2** was isolated as a white solid. Yield: 95 mg, 88%.^{1}H NMR ($(CD_3)_2CO$): 7.71 (s, 1H), 7.49 (d, 2H, $^{3}J_{ortho}$ 7.3 Hz), 7.43 (dd, 1H, $^{3}J_{ortho}$ 7.3 Hz), 7.02 (s, 4H), 6.85 (s, 1H), 6.79 (s, 1H), 5.18 (s, 4H), 3.63 (t, 8H, THF), 3.06 (s, 8H), 1.79 (t, 8H, THF), 1.34 (s, 6H), 1.32 (s, 6H), –2.28 (s, 4H). ^{13}C NMR ($(CD_3)_2CO$): 158.57, 144.10, 138.09, 128.44, 127.25, 123.90, 122.58, 112.15, 69.50, 68.07, 61.96, 54.11, 42.80, 42.70, 26.15, 22.51. ^{11}B NMR ($(CD_3)_2CO$): –6.05 (s, 1B), –7.19 (s, 2B), –13.38 (s, 2B), –16.41 (s, 1B), –17.38 (s, 1B), –31.74 (s, 1B), –34.20 (s, 1B). IR (KBr, cm^{-1}): 3033 ν(C–H_{aryl}), 2931 ν(C–H_{alkyl}), 2518 ν(B–H), 1627, 1404, 1008. Elemental Analysis Calcd (%) for $C_{36}H_{74}B_{36}K_4O_2{\cdot}2(C_4H_8O)$: C 43.03; H 7.33. Found: C 42.75; H 7.52.

Synthesis of *nido*-4

The procedure was the same as for *nido*-**3**, using *closo*-**2**. Yield: 119 mg, 95%. ^{1}H NMR ($(CD_3)_2CO$): 7.73 (s, 1H), 7.58 (d, 2H, $^{3}J_{ortho}$ 7.5 Hz), 7.47 (dd, 1H, $^{3}J_{ortho}$ 7.5 Hz), 7.02 (s, 4H), 6.80 (s, 1H), 6.74 (s, 1H), 5.20 (s, 4H), 3.36 (s, 48H), 3.09 (s, 8H), 1.34 (s, 6H), 1.33 (s, 6H), –2.41 (s, 4H). ^{13}C NMR ($(CD_3)_2CO$): 159.18, 144.87, 138.18, 129.41, 126.43, 124.04, 123.53, 113.42, 70.26, 55.82, 43.37, 43.24, 23.88. ^{11}B NMR ($(CD_3)_2CO$): –5.92 (s, 1B), –7.06 (s, 2B), –13.52 (s, 2B), –17.43 (s, 2B), –31.81 (s, 1B), –34.17 (s, 1B). IR (KBr, cm^{-1}): 3033 ν(C–H_{aryl}), 2929 ν(C–H_{alkyl}), 2515 ν(B–H), 1589, 1483, 1026. Elemental Analysis Calcd (%) for $C_{52}H_{122}B_{36}N_4O_2$: C 50.95; H 9.96; N 4.57. Found: C, 51.25; H, 10.13; N, 4.40.

Synthesis of *nido*-5

The degradation procedure was the same as for *nido*-**1**, using *closo*-**3** (100 mg, 0.18 mmol) and KOH (40 mg 0.72 mmol). Compound *nido*-**5** was isolated as a white solid. Yield: 90 mg, 84%. ^{1}H NMR ($(CD_3)_2CO$): 7.22 (s, 4H), 6.94 (m, 7H), 6.85 (s, 2H), 5.99 (d, 1H), 3.63 (t, 8H, THF), 2.59 (d, 1H, $^{2}J_{gem}$ 14.9 Hz), 2.57 (d, 1H, $^{2}J_{gem}$ 14.9 Hz), 2.46 (d, 1H, $^{2}J_{gem}$ 14.9 Hz), 2.45 (d, 1H, $^{2}J_{gem}$ 14.9 Hz), 1.79 (t, 8H, THF), –1.95 (s, 2H). ^{13}C NMR ($(CD_3)_2CO$): 144.62, 143.77, 141.96, 141.22, 135.33, 135.02, 133.75, 132.84, 129.12, 128.52, 127.98, 127.47, 127.09, 126.84, 126.01, 69.18, 68.07, 65.22, 44.96, 43.21, 26.15. ^{11}B NMR ($(CD_3)_2CO$): –7.81 (s, 1B), –8.82 (s, 1B), –12.44 (s, 1B), –16.44 (s, 2B), –17.85 (s, 2B), –32.93 (s, 1B), –35.58 (s, 1B). IR (KBr, cm^{-1}) 3055 ν(C–H_{aryl}), 2923 ν(C–H_{alky}), 2518 ν(B–H), 1753, 1602, 1442. Elemental Analysis Calcd (%) for $C_{24}H_{38}B_{18}K_2{\cdot}2(C_4H_8O)$: C 51.30; H 7.30. Found: C 50.92; H 7.45.

Synthesis of *nido*-6

The degradation procedure was the same as for *nido*-**1**, using *closo*-**4** (100 mg, 0.18 mmol) and KOH (40 mg 0.72 mmol). Compound *nido*-**6** was isolated as a white solid. Yield: 100 mg, 91%.^{1}H NMR ($(CD_3)_2CO$): 7.49 (t, 1H, ^{3}J 7.7 Hz), 7.37 (d, 1H, ^{3}J 7.7 Hz), 7.31

(d, 1H, ^3J 7.7 Hz), 7.22 (m, 4H), 6.82 (m, 6H), 3.63 (t, 4H, THF), 2.80 (d, 1H, $^2J_{gem}$ 16.8 Hz), 2.75 (d, 1H, $^2J_{gem}$ 16.8 Hz), 2.61 (d, 1H, $^2J_{gem}$ 16.8 Hz), 2.55 (d, 1H, $^2J_{gem}$ 16.8 Hz), 1.79 (t, 4H, THF), –1.92 (s, 2H). ^{13}C NMR ($(CD_3)_2CO$): 160.35, 159.95, 141.99, 134.34, 132.25, 132.16, 126.34, 126.33, 125.19, 125.07, 120.18, 68.07, 67.17, 65.20, 44.98, 44.81, 26.15. ^{11}B NMR ($(CD_3)_2CO$): –7.97 (2B), –12.23 (1B), –14.20 (1B), –17,50 (3B), –32.53 (1B), –35.25 (1B). IR (KBr, cm^{-1}): 3056 ν(C–H$_{aryl}$), 2927 ν(C–H$_{alky}$), 2518 ν(B–H), 1627, 1400, 1006. Elemental Analysis Calcd (%) for $C_{23}H_{37}B_{18}K_2N\cdot(C_4H_8O)$: C 48.25; H 6.69; N 2.08. Found: C 48.24; H 6.49; N 2.32.

Synthesis of *nido*-7

The procedure was the same as for *nido*-**3**, using *closo*-**3**. Yield: 116 mg, 96%. ^{1}H NMR ($(CD_3)_2CO$): 7.25 (s, 4H), 6.96 (m, 6H), 6.82 (s, 3H), 6.13 (d, 1H), 3.37 (s, 24H), 2.59 (d, 1H, $^2J_{gem}$ 14.9 Hz), 2.57 (d, 1H, $^2J_{gem}$ 14.9 Hz), 2.48 (d, 1H, $^2J_{gem}$ 14.9 Hz), 2.47 (d, 1H, $^2J_{gem}$ 14.9 Hz), –1.98 (s, 2H). ^{13}C NMR ($(CD_3)_2CO$): 143.53, 142.96, 141.56, 141.59, 133.13, 133.08, 132.24, 131.77,128.24, 127.39, 127.34, 127.22, 127.16, 126.94, 125.89, 68.28, 64.16, 55.86, 43.06, 42.97. ^{11}B NMR ($(CD_3)_2CO$): –7.66 (s, 1B), –8.77 (s, 1B), –12.26 (s, 1B), –16.29 (s, 2B), –17.79 (s, 2B), –32.80 (s, 1B), –35.43 (s, 1B). IR (KBr, cm^{-1}): 3029 ν(C–H$_{aryl}$), 2916 ν(C–H$_{alkyl}$), 2518 ν(B–H), 1483, 946. Elemental Analysis Calcd (%) for $C_{32}H_{62}B_{18}N_2$: C 57.40; H 9.26; N 4.18. Found: C, 56.62; H, 9.18; N, 4.05.

Synthesis of *nido*-8

The procedure was the same as for *nido*-**3**, using *closo*-**4**. Yield: 116 mg, 95%. ^{1}H NMR ($(CD_3)_2CO$): 7.27 (t, 1H, ^3J 7.7 Hz), 7.07 (d, 1H, ^3J 7.7 Hz), 7.01 (d, 1H, ^3J 7.7 Hz), 6.67 (m, 4H), 6.42 (m, 6H), 2.82 (s, 24H), 2.75 (d, 1H, $^2J_{gem}$ 16.8 Hz), 2.65 (d, 1H, $^2J_{gem}$ 16.8 Hz), 2.54 (d, 1H, $^2J_{gem}$ 16.8 Hz), 2.43 (d, 1H, $^2J_{gem}$ 16.8 Hz), –2.62 (s, 2H). ^{13}C NMR ($(CD_3)_2CO$): 159.53, 158.92, 141.90, 132.06, 125.23, 124.09, 120.22, 67.17, 65.20, 55.64, 43.82, 42.91. ^{11}B NMR ($(CD_3)_2CO$): –8.67 (2B), –13.73 (1B), –15.20 (1B), –18.00 (3B), –32.97 (1B), –35.58 (1B) IR (KBr, cm^{-1}): 3044 ν(C–H$_{aryl}$), 2926 ν(C–H$_{alkyl}$), 2518 ν(B–H), 1634, 1412, 946. Elemental Analysis Calcd (%) for $C_{31}H_{61}B_{18}N_3$: C 55.48; H 9.10; N 6.26. Found: C 54.70; H 9.15; N 6.10.

X-ray crystallographic study of *closo*-3

The crystals were obtained in acetone. Crystallographic data were collected at 173 K with a Nonius-Kappa CCD area detector diffractometer, using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). The data sets were corrected for absorption using SADABS.[23a] The structure was solved by direct methods by use of the SHELXS-97 program.[23b] The full-matrix, least-squares refinements on F^2 were performed using SHELXL-97 program.[23b] The CH and BH hydrogen atoms were included at fixed distances with the fixed displacement parameters from their host atoms.

Crystal data for *closo*-**3**: $C_{24}H_{38}B_{20}$, M_r = 542.74, monoclinic, $C2/c$, a = 33.7783(14) Å, b = 7.6998(2) Å, c = 26.8231(13) Å, b = 116.055(3), V = 6267.3(4) Å^3, Z = 8, ρ_{calc} = 1.150 g cm^{-3}, μ(Mo-Kα) = 0.055 mm^{-1}, $F(000)$ = 2256, θ_{max} = 25.25°, 10454 reflections, 5650 independent reflections (R_{int} = 0.104), R_1 = 0.125, wR_2 = 0.298 for 397 parameters with reflections $I > 2\sigma(I)$. CCDC 802843.†

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