A Series of Ultra-Efficient Blue Borane Fluorophores.

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Abstract

We present the first examples of alkylated derivatives of the macropolyhedral boron hydride, *anti*-B₁₈H₂₂ – which is the gain medium in the first borane laser. This new series of ten highly-stable and colourless organic-inorganic hybrid clusters are capable of the conversion of UVA irradiation to blue light with fluorescence quantum yields of unity. This study gives a comprehensive description of their synthesis, isolation and structural characterization together with a delineation of their photophysical properties using a combined theoretical and experimental approach. Treatment of *anti*-B₁₈H₂₂ **1** with RI (where R = Me or Et) in the presence of AlCl₃ gives a series of alkylated derivatives, R_x-*anti*-B₁₈H_{22-x} (where x = 2 to 6), compounds **2-6**, in which the 18-vertex octadecaborane cluster architectures are preserved and yet undergo a linear “polyhedral swelling”, depending on the number of cluster alkyl substituents. The use of dichloromethane solvent in the synthetic procedure leads to dichlorination of the borane cluster and increased alkylation to give Me₁₁-*anti*-B₁₈H₉Cl₂ **11**, Me₁₂-*anti*-

$B_{18}H_8Cl_2$ **12** and Me_{13} -*anti*- $B_{18}H_7Cl_2$ **13**. All new alkyl derivatives are highly stable, extremely efficient ($\Phi_F = 0.76 - 1.0$) blue fluorophores ($\lambda_{ems} = 423 - 427$ nm) and are soluble in a wide range of organic solvents and also a polystyrene matrix. The Et_4 -*anti*- $B_{18}H_{18}$ derivative **4b** crystallizes from pentane solution in two phases, with consequent multi-absorption and multi-emission photophysical properties. An ultra-fast transient UV-vis absorption spectroscopic study of compounds **4a** and **4b** reveals that an efficient excited-state absorption at the emission wavelength inhibits the laser performance of these otherwise remarkable luminescent molecules. All these new compounds add to the growing portfolio of octadecaborane-based luminescent species, and, in an effort to broaden the perspective on their highly-emissive photophysical properties, we highlight emerging patterns in the influence that successive substitutions have on the molecular size of the 18-vertex borane cluster structure and distribution of electron density within.

Introduction

There is a demand in the fields of optoelectronic devices, energy conversion, luminescence sensing and bioimaging, and photodynamic therapy, for efficient solution-processed blue-luminescent materials. Here, there is renewed interest in the binary boron hydride cluster compound *anti*- $B_{18}H_{22}$ **1** due to the discovery of its utility as a new class of laser material.¹ It is also of particular interest as it fluoresces in the elusive blue region of the spectrum with a quantum yield approaching unity,² it is highly photostable,¹ and it is readily soluble in organic polymer matrices.¹ These are all factors of general practical benefit regarding the fabrication of optical devices. The photophysics of compound **1** may be modified by the introduction of substituents or ligands to replace the terminal hydrogen atoms on the cluster such as $-SH$,³ bromine,⁴ iodine,⁵ and pyridine^{6, 7} to give molecules capable of, for example, environment-sensitive thermochromic luminescence,⁶ single-molecule multiple emissions,⁴ and the photosensitization of oxygen.⁵ In addition, the optical properties of the parent compound have been shown to tolerate dissolution in aqueous micelles,^{8, 9} in work that has been recently patented.¹⁰ Previously, luminescence from **1** in water had been unachievable due to insolubility of its neutral form and the non-luminescent nature of its anion $[B_{18}H_{21}]^-$, which, in aqueous environments, is readily generated through deprotonation of one of the compound's highly acidic¹¹ bridging hydrogen atoms. For reasons of enhancing solubility, reducing acidity, and rationalizing the modification of the photophysical properties of the underlying cluster, we too are interested in covering the periphery of the molecule **1** with a protective sheath. However, in our case, the intention is to incorporate the sheath as an integral part of the molecule. To this end, we are pioneering synthetic procedures to the formation of hitherto elusive boron-carbon bonds on the *anti*-octadecaborane cluster and the peralkylation of compound **1** in order to investigate effects on its structural and photophysical properties.

Results and Discussion

1. Syntheses and structural characterization

Stirring *anti*-B₁₈H₂₂ (**1**) with excess AlCl₃ and MeI for two weeks in a round-bottom flask sealed with a Teflon stopcock, followed by recrystallization from hot *n*-hexane, gives 3,3',4,4'-Me₄-*anti*-B₁₈H₂₂ (**4a**) as the main product in 14 % yield (Equation 1; the cluster numbering for *anti*-B₁₈H₂₂ and the derivatives described here is shown in schematic structure in Figure 1) together with a number of lower-yield products with two, three, five and six methyl substituents. The products were isolated by a combination of thin-layer chromatography (TLC) and fractional crystallization. In a similar reaction with EtI, one main product was isolated and characterized similarly as 3,3',4,4'-Et₄-*anti*-B₁₈H₁₈ (**4b**), in a higher yield of 27 %. Other minor products were present in this reaction mixture, but they were less prominent than in the methylated case and were not isolated. To aid the reader and for clarity, with the exception of the initial compound **1**, the compound number represents the number of alkyl group substituents on the cluster. Different isomers with the same number of alkyl substituents or different alkyl group identity are labelled **a** or **b**.

These reactions were carried out with an excess of the alkyl iodide, which also acted as the solvent. The use of propyl iodide, benzyl iodide and phenyl iodide resulted in no alkylation or arylation but led instead to iodination and the formation of known 4,4'-I₂-B₁₈H₂₀.⁵ Additionally, it may be noted that reaction with methyl iodide at elevated temperatures, in an attempt to speed up the reaction, resulted in mixtures with up to 10 methyl groups as shown by high-resolution mass spectrometry (see Table 1), but these also held iodine substituents. Previous work on iodinated octadecaborane⁵ showed that the presence of iodine shifts phosphorescence emissions away from blue toward green and we have therefore not yet followed up this line of enquiry. When carried out in the additional presence of dichloromethane solvent at ambient temperature the reaction progresses to a higher degrees of alkylation and produces a range of products, which have been described in a preliminary communication.¹² These are dealt with in more detail later.

Table 1. HRMS data for iodinated and methylated compounds.

	Measured	Calculated
C ₂ H ₂₅ B ₁₈	244.3751	244.3747
C ₃ H ₂₇ B ₁₈	258.3893	258.3905
C ₄ H ₂₉ B ₁₈	272.4062	272.4061
C ₁₀ H ₄₀ B ₁₈ I ₁	482.3924	482.3971

$C_9H_{38}B_{18}I_1$	468.3758	468.3814
$C_8H_{36}B_{18}I_1$	454.3604	454.3657

Boron-11 NMR spectroscopy of the product mixture indicated that the compounds were present in significantly higher overall yields, but, due to the small differences in the solubilities between the compounds with different degrees of substitution and the different structural isomers between some of these, the isolated yields we report here were lower than if optimized, but together they form an interesting series of alkylated octadecaborane cluster compounds containing from two to six methyl groups. Relatively low yields for some of the derivatives do not present a significant impediment at this stage, as the compounds are so highly emissive that only nanomolar solutions are required to brightly manifest their luminescent properties. On this point it is also worth emphasizing the high stability of the new compounds, as their constitution and properties do not change even after repeated melting at 200 °C or exposure to refluxing hydrocarbon solvents.

Di- to hexa-alkylation of *anti*-B₁₈H₂₂. In total, seven methylated compounds were characterized by NMR spectroscopy, mass spectrometry, and in most cases by single-crystal X-ray diffraction studies. These were: 4,4'-Me₂-*anti*-B₁₈H₂₀ (**2**), 3,4,4'-Me₃-*anti*-B₁₈H₁₉ (**3a**), 3,3',4-Me₃-*anti*-B₁₈H₁₉ (**3b**), 3,3',4,4'-Me₄-*anti*-B₁₈H₁₈ (**4a**), 1,3,3',4,4'-Me₅-*anti*-B₁₈H₁₇ (**5a**), 3,3',4,4',8-Me₅-*anti*-B₁₈H₁₇ (**5b**) and 1,1',3,3',4,4'-Me₆-*anti*-B₁₈H₁₆ (**6**). NMR data are listed in Tables S1 to S5 of the Supporting Information and a stacked plot of the ¹¹B-{¹H} NMR spectra is shown in Figure 1 (to aid the quick identification of these new species for those interested in their repeat synthesis, key NMR spectra for compounds **3-6** are shown in the Supporting Information, Figures S1 – S28). Assignments in Tables S1-S5 are made by a comparison of the chemical shifts with *anti*-B₁₈H₂₂ and its derivatives, which have been well-characterized by ¹¹B and ¹H NMR spectroscopy,¹³ together with HMQC (Heteronuclear Multiple-Quantum Correlation) experiments that correlate the bridging hydrogen atoms and the boron atoms to which they are attached. These are all confirmed by DFT/GIAO calculations of boron chemical shifts at the computationally economical B3LYP/6-31G* methodology and basis set level.¹⁴ It may be noted that there is an excellent correspondence between the measured and calculated GIAO values, which are within 2 ppm of each other, and that the good correspondence extends even to the proton chemical shifts. Although the calculated proton data are not as accurate as those for boron, and do not reproduce the measured values as precisely, the ordering of the chemical shifts exactly parallels the measured values. Single crystals were obtained for all of these compounds with the exception of **6**, but in the cases of **3b** and **5a**, disorder over a crystallographic inversion centre with regard to the methyl group positions makes the measured geometrical parameters less precise for comparison with the calculated separations and thus only the single-crystal X-ray structures for compounds **2**, **3a**, **4a** and **5b** are shown in Figure 2, accompanied by the structure for tetraethylated derivative **4b** in Figure 3. Tables of geometrical parameters together with their DFT-

calculated geometries are listed in the Supporting Information Tables S6 and S7. The vast majority of the calculated interboron distances are within a maximum of three standard uncertainties of the measured values, thus paralleling the close correspondence of the calculated and measured boron NMR chemical shifts. This goes to support the validity of correlations made later between the number of cluster methyl substituents and the resultant calculated expanded volume of the cluster (our general approach in our work using quantum mechanical calculations is to continually verify them with experiment and never to get too far away from an experimental measurement in our theoretical rationalizations of the data).

Figure 1. Stacked plot of $^{11}\text{B}\{-^1\text{H}\}$ spectra for compounds 2 to 6 with labels on the upper spectrum representing the cluster vertex assignments. Side-on (lower left) and aerial (upper left) perspectives of compound 1 including numbering.

Figure 2. Molecular structures of compounds **2**, **3a**, **4a** and **5b** as determined by single-crystal X-ray diffraction analyses. Displacement ellipsoids for non-hydrogen atoms are drawn at a 50% probability level. Molecules have crystallographic inversion symmetry; hence the asymmetric unit is half a molecule.

Figure 3. The molecular structure of **4b**. Displacement ellipsoids for non-hydrogen atoms are drawn at a 50% probability level. The borane cage is located on an inversion centre between B5 and B5'/B6.

Extensive methylation of *anti*-B₁₈H₂₂. Use of the same synthetic method as for the preparation of compounds **2-6**, but with the addition of dichloromethane solvent, led to dichlorination of the 18-vertex cluster and more extensive methylation, resulting in the eventual isolation of undecamethylated 2,2'-Cl₂-1,1',3,3',4,4',7,7',8,8',10,10'-Me₁₁-*anti*-B₁₈H₉ (compound **11**), dodecamethylated 2,2'-Cl₂-1,1',3,3',4,4',7,7',8,8',10,10'-Me₁₂-*anti*-B₁₈H₈ (compound **12**), and the tridecamethylated 2,2'-Cl₂-1,1',3,3',4,4',7,7',8,8',9,10,10'-Me₁₃-*anti*-B₁₈H₇ (compound **13**). Details of the synthesis and structural characterization of compounds **12** and **13** are the focus of a recent communication.¹² Subsequently, the undecamethylated product **11** has been characterized by single-crystal X-ray diffraction and a drawing of the structure is shown in Figure 4. In this compound the B9, B9', B10 vertices remain unmethylated. However, compound **13**, it may be noted, does show methylation in the B9 position thus indicating that all positions on the cluster are potentially available for substitution. Separation of these closely related compounds is difficult and thus solid solutions are often a consequence. Compound **11** is such a case, the sample here, according to the crystallographic study, consisting of a mixture of **11** and **12** in a 60:40 ratio, respectively, whereas **13** shows no evidence of other constituents. Unfortunately, isolated amounts of **11** and **13** were insufficient for further NMR characterization or analysis of their photophysical properties.

Figure 4. ORTEP-3¹⁵ drawing of the cluster structure of one of the two independent molecules in the asymmetric unit of **11** and of **12**¹² illustrating the interaction between the chlorine substituent and H(9,10).

The seeming ability of dichloromethane solvent to facilitate further cluster methylation reflects previous observations in carbaborane chemistry, in which extensive methylation of the *ortho*-isomer of C₂B₁₀H₁₂ was made possible only by cluster-substitution with electron-rich halogen atoms that ‘pump’ electron density into the boron cluster, counterbalancing the electron-withdrawing effect of the methyl substituents, and thus facilitating further cluster methylation.¹⁶ A point of note in the proton NMR spectrum of **12**, not made in the initial communication, is that the resonance at +0.83 ppm, due to the μH(9,10) bridging protons, is considerably deshielded when compared to that in other

octadecaborane compounds, such as *anti*-B₁₈H₂₂, **1**, itself, where it appears at $\delta(^1\text{H})$ -0.38 ppm.¹³ The other bridging protons, at -0.52 and -1.79 ppm, are in comparatively normal chemical shift positions, thereby suggesting that the deshielding of $\mu\text{H}(9,10',9',10')$ is not due to the presence of the adjacent methyl groups. The difference may be ascribed to an interaction between the chlorine substituent on B2 and the bridging hydrogen $\mu\text{H}(9,10)$ atom (Figure 4 dashed line) that is either hydrogen bonding,¹⁷ electrostatic or predominantly dispersive¹⁸ in its nature. Their measured interatomic separation of $2.36(3)$ Å (2.33 Å, calculated) is notably lower than the 2.95 Å sum of the van der Waals radii of the atoms. In the parent borane, this chemical shift of $\mu\text{H}(9,10)$, viz. (^1H), -0.38 ppm, is also considerably to lower field compared to the adjacent $\mu\text{H}(8,9)$ proton at -2.87 ppm. This difference may thus be a combination both of the slightly different cluster position relative to the other subcluster, together with the interaction between the $\mu\text{H}(9,10)$ proton and the terminal proton on B(2) which are separated by $2.11(2)$ Å in the crystal, and which is also less than the sum of the van der Waals radii, 2.4 Å. It was previously postulated,¹³ from a consideration of the aromatic-solvent-induced chemical shift (ASIS) change of $+0.58$ ppm in the proton chemical shifts between CD₂Cl₂ and C₆D₆ solutions of *anti*-B₁₈H₂₂, that the $\mu\text{H}(8,9)$ bridging proton might undergo a weak interaction with the aromatic solvent similar to that seen in *nido*-B₁₀H₁₄,¹⁷ and this has been subsequently confirmed in the crystal structures of the benzene solvates of *anti*-B₁₈H₂₂,¹⁸ 4,4'-(SH)₂-*anti*-B₁₈H₂₀,³ and 4,4'-I₂-*anti*-B₁₈H₂₀.⁵ This $+0.58$ ppm change in **1** compares to the effective $+1.21$ ppm difference in the chemical shift of $\mu\text{H}(9,10)$ in **12** ($0.83 + 0.38 = 1.21$ ppm). This may be a consequence both of the considerably closer approach of the internally structurally constrained Cl and H positions for $\mu\text{H}(9,10)$, 2.33 Å, and of the electronegativity of chlorine, compared to that for $\mu\text{H}(8,9)$ and the benzene ring centroid in *anti*-B₁₈H₂₂.C₆H₆ of 2.816 Å.¹⁸

2. Further considerations of structural aspects

In all the new compounds **2-6** and **11-13**, the basic octadecaborane cluster architecture of two decaboranyl sub-units fused by a two-boron atom shared edge is preserved (see schematic in Figure 1). Structural changes are therefore limited to just the number and position of substituents on the 18-vertex boron skeleton. This has permitted us the opportunity to use the NMR, X-ray, and computed data to investigate emerging patterns or trends in the geometries and electronic structure of the alkylated derivatives. What follows is a presentation of what we regard as relevant deductions from this data analysis.

Cluster-only Total Deshielding. Since magnetic nuclear shielding depends ultimately and directly on molecular orbital (MO) structure, then changes in shielding pattern imply a change in the MO structure. As we are particularly interested in the photophysics of the new molecules, in which MO structure is of paramount importance, it is instructive to compare the ^{11}B shielding patterns.

Figure 5. Comparison of ^{11}B NMR chemical shift data for all new symmetrical alkylated derivatives of *anti*- $\text{B}_{18}\text{H}_{22}$ (**1**), compounds **2**, **4a**, **4b**, **6** and **12**.

Figure 5 is such a comparison of ^{11}B NMR chemical shifts for all the new symmetrical alkylated derivatives of *anti*- $\text{B}_{18}\text{H}_{22}$, compounds **2**, **4a**, **4b**, **6** and **12**. Generally, there is a trend in the deshielding (shift to more positive ^{11}B chemical shift) of almost all the boron nuclei to the external magnetic field with increasing alkylation, but especially at the substituted positions. This deshielding effect is a consequence of the alkyl groups pulling electron density from the boron atoms, thus increasing the effective force of the external magnetic field to their nuclei and, therefore, the energy difference between the boron nuclei spin-states. With progressive alkylation, subtle fluctuations in this trend are, however, apparent. For example, when considering the B3,3' position (black trace in Figure 5), methylation at the neighbouring B4,4' position causes a deshielding of the B3,3' nuclei by 4.1 ppm, which is subsequently more than doubled, by a further 8.9 ppm, from the next methylation at its position. However, further methylation at the neighbouring B1,1' position results in a smaller increase in the deshielding of the B3,3' nuclei by just 1.1 ppm, and an additional six cluster methylations, to give compound **12**, actually leads to a reversal in the trend, and a reduction in the deshielding experienced by the B3,3' nuclei by -3.1 ppm. The B1,1' position seems to follow a similar pattern.

The data, therefore, provide interesting insights both into the individual local atomic environments of the 18-vertex boron cluster, but also into the molecule as a whole. Here, it is useful to make a sum of the collective deshieldings of all boron nuclei in each compound to give what we have termed a Cluster-only Total Deshielding (CTD) value. These CTD values for individual molecules may then be compared to reveal the combined effect of increasing number of alkyl substituents on the octadecaborane cluster. Such summations are shown for compounds **2**, **4a**, **4b**, **6** and **12** in Figure 6.

The data are normalized to *anti*-B₁₈H₂₂ and show a steady, albeit non-linear, increase in the CTD with respect to an increasing number of cluster substitutions. This translates to a progressive abstraction of electron density from the boron cluster towards the external alkyl “sheath” around the outside of the molecule. The deshielding apparent in the NMR, *i.e.* the withdrawal of electron density from the cluster, is not, however, directly proportional to the number of alkyl substituents and the first dialkylation in compound **2** results in a disproportionately higher deshielding compared to subsequent alkylations.

Figure 6. Trend in Cluster-only Total Deshielding for compounds **2**, **4a**, **4b**, **6** and **12**.

Cluster-only Total Charge. A related parameter to changes in magnetic shielding is that of electron distribution in the boron cluster, for which a good estimation can be made using a calculated Natural Population Analysis, the results of which are summarized in Figure 7 and Figure S29 (our study is limited to the four symmetrical methylated derivatives, **2**, **4a**, **6** and **12**). The data clearly show a shift in electron distribution from the boron cluster towards the methyl groups on each alkylation, which, as expected, reflects the trend in nuclear shielding data discussed above.

Figure 7. Calculated Natural Populations for symmetrical methylated derivatives of *anti*-B₁₈H₂₂ (**1**), compounds **2**, **4a**, **6** and **12**.

The combined effect of all methylations on the boron clusters of compounds **2**, **4a**, **6** and **12** may be conveniently assessed by comparison of the summation of all boron Natural Populations for each compound to give what is termed the “Cluster-only Total Charge” of the molecule (CTC).¹⁶ Figure 8 shows the trend in increasing CTC relative to increasing number of methylations, which shows a greater linearity than the increasing Cluster-only Total Deshielding discussed above.

Figure 8. Cluster-only Total Charge for symmetrical methylated derivatives of *anti*-B₁₈H₂₂, compounds **2**, **4a**, **6** and **12**.

Thus, we see increasing evidence for the movement of electron density from the boron cluster towards its alkyl periphery. This electronic phenomenon also manifests in the overall size of the octadecaboranyl skeleton of the molecules inducing a ‘swelling’ in cluster volume.

Swollen polyhedral cluster volume: In cluster boron and metallaborane chemistry it has been a convention to describe changes in the geometry of the cage due to substituents or other effects by delineating changes in interatomic distances or angles. In previous work^{2,3,12} we noted that the calculated excited-state molecular geometries exhibited a notable increase in the size of some cage boron-boron connections relative to the ground states. This sparked an interest to look into a global change in the cluster volume of the ground state and excited states of the molecules rather than to point out variations in individual intracluster vectors. To this end, in our initial communication¹² on dodecamethylated derivative **12**, we used, as a proxy for the overall increase in cluster size resulting from alkyl group introduction, a summation of the boron-boron interatomic separations in one subcluster. Here, we now show in Figure 9 plots of the summed interboron distances for one subcluster in a range of calculated methyl substituted octadecaborane compounds together with data for the methylated derivatives of **1** obtained from single-crystal X-ray studies. An inspection of the plot shows a good correlation between the data for the derivatives of **1** obtained from single-crystal X-ray studies and those derivatives for which DFT-calculated geometries were used. The data for compounds **3b** and **5a** are not included in the measured values, as these structures were disordered

across the inversion centre, and this would, in these clusters with odd numbers of three or five substituents over the two halves of the molecule, give an average value for the two sides.

Figure 9. Subcluster volume *versus* number of methyl substituents: red squares for calculated geometries; blue diamonds measured from X-ray single-crystal data for compounds **1**,¹⁸ **2**, etc; green triangle for the calculated compound **12**, and black diamond the S_1 -minimum for **1**.²

The data show a reasonably linear correlation between cluster swelling and the increasing number of methyl substituents. The chlorine substituents appear to have a similar effect to the methyl groups. The trend is of interest as the swelling might be expected to perturb the precise photophysical properties of the molecule in comparison to *anti*- $B_{18}H_{22}$, potentially allowing a tuning of the properties. The extent of the polyhedral swelling in compound **12** in the ground state is very similar to that of the sum of interboron distances for the calculated excited state of compound **1**.² This is a correlation of potential fundamental significance and one we hope, in the light of the growing portfolio of luminescent derivatives of *anti*- $B_{18}H_{22}$, will provide important insights for eventual molecular property design.

3. Optoelectronic properties

Photophysical properties. Figure 10 and Table 2 summarize the ground-state absorption (GSA) and emission characteristics of new compounds **2**, **3a**, **4a**, **4b**, **5a** and **12** in hexane solutions. Their spectra are superimposed onto those for **1** (black curves) as reference, and reveal a general bathochromic trend. The emissions from all alkylated derivatives are uniformly red-shifted by about 15 nm with respect to that for **1**. The GSA characteristics of the new molecules in solution show more variation than do their emissions, but the general absorption signature is similar to that for **1**. The exception is that the highly methylated compound **12** displays the greatest bathochromic shift for its two absorption bands (of 14 nm and 29 nm respectively) and it also exhibits a measurable increase in absorption efficiency.

Figure 10. UV/vis absorption spectra (above) and normalized fluorescence (below) of compounds **1**, **2**, **3a**, **4a**, **4b**, **5a** and **12** in hexane.

The fluorescence quantum yields, Φ_F , remain essentially at unity for all derivatives, with the exception of compound **12** that gives an efficiency of 0.76. A further trend apparent from the data is that the increasing extent of alkylation correlates to a gradual shortening of excited state lifetimes.

Table 2. Properties of substituted *anti*-B₁₈H₂₂ in hexane at room temperature.^a

compound	λ_{abs}/nm	λ_F/nm	τ_F/ns	Φ_F
1	273, 328	410	11.2	0.97 ^b
2	283, 337	423	11.6	0.96
3a	285, 335	423	11.2	1.0
4a	289, 335	424	10.8	1.0
4b	290, 337	427	10.8	1.0
5a	290, 337	425	10.7	1.0

12	287, 357	426	8.4	0.76
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^a λ_{abs} are the maxima of the absorption bands; λ_F is the maximum of the fluorescence band; τ_F is the fluorescence lifetime, excited at 337 nm, emission wavelength at the maximum of the fluorescence band; Φ_F is the fluorescence quantum yield, excitation wavelengths were 320, 330 and 340 nm). ^b From reference 2.

It is important here to emphasize that in contrast to compounds **1-6**, compound **12** has two chlorine substituents in addition to its methyl groups, and it is reasonable that these two halogen atoms are a main factor in the difference in absorption and emission properties. The calculated HOMO for **12** (see Figure 11) shows contributions from the chlorine atoms, which also play a role in the cluster electronics as evidenced in both the Cluster-only Total Charge and the Cluster Polyhedral Volume as discussed above. The reduction in Φ_F suggests that the presence of the two chlorine substituents in **12** create alternative deactivation pathways to its excited-state other than fluorescence. The precise nature of these other deactivation pathways is unclear; however intersystem crossing (ISC) to low-lying triplet states is unlikely as no phosphorescence was observed. Therefore, a non-radiative pathway, presumably based on a lowering in the energy barrier from the S_1 excited-state minimum of the system to its conical intersection point with the ground state, is the most probable reason. A solid relationship between the accessibility of S_1/S_0 crossing points and its implications on the emission properties have been established for closely related systems.^{3, 6, 7, 19}

Figure 11. A plot of calculated HOMO-LUMO energy differences ($\Delta E(H-L)$) against increasing number of substituents, including HOMO and LUMO orbital diagrams for compounds **2**, **3a**, **4a**, **4b**, **5b**, **11**, **12**, and **13**.

HOMO and LUMO energies for all new compounds for which we have X-ray crystallographic data (i.e. compounds **2**, **3a**, **4a**, **4b**, **5b**, **11**, **12**, and **13**) have been calculated, and a plot these energy differences against their number of alkyl substituents, along with graphical depictions of the relevant

orbitals, are shown in Figure 11. A comparison of these orbital diagrams with those already published² for compound **1** suggests that the molecular orbitals involved in luminescence from the new alkyl-derivatives **2-5** are very similar to those for *anti*-B₁₈H₂₂ in that they pervade both sub-clusters of the borane cluster and are of similar general shape and configuration. This permits the conclusion that the photoactive unit of these derivatives is their {B₁₈}-cluster core, with smaller contributions to the HOMOs from the alkyl substituents. The chlorine substituents in compounds **11-13** seem to have a greater contribution to these compounds' HOMOs, possibly explaining the marked difference in absorption properties of compound **12** compared to those of **1-6**.

Figure 12 focuses on the two main products, compounds **4a** and **4b**, showing not only the HOMO and LUMO at the ground-state (Franck-Condon) region, but also at their S₁ minima (also “hot” S₀ if we consider the extremely fast light emission), which characterize the emission from these compounds. Once again, it is clear that it is the {B₁₈}-cluster core that is the major protagonist in the emission process with only minor contribution from the alkyl substituents.

Figure 12. A plot of calculated HOMO-LUMO energy differences ($\Delta E(H-L)$) including HOMO and LUMO orbital diagrams for compounds **4a**, **4b**.

Laser experiments. Compound **1** is a photostable blue laser source.¹ As the new alkylated derivatives described here have impressive quantum yields of fluorescence equal to compound **1** and, indeed, slightly superior absorption efficiencies, we were keen to investigate their laser properties. Of the

derivatives described here, compounds **4a** and **4b** were selected as the most appropriate subjects for this study owing to their relative ease of synthesis and isolation in reasonable yields. However, under the same experimental conditions used previously for **1**,¹ neither **4a** nor **4b** displayed laser emission, irrespective of the sample concentrations used. Nevertheless, at the highest concentrations of both compounds, there is some degree of narrowing of the emission band (see Figure S 30 in the SI), meaning that stimulated emission and amplification is starting to occur. However, when the pump energy was increased (2.2 mJ) to see if the laser threshold could be achieved, no lasing was observed.

An understanding of why solutions of compounds **4a** and **4b** do not lase is an obvious crucial step in the improvement on the laser performance of **1**. Here, a number of considerations may be taken into account to explain this unexpected contradictory behavior. Firstly, the fluorescence quantum yields of 1.0 for both compounds imply that there are no competing relaxation pathways for their molecules in the S₁ excited-state other than blue fluorescence. Secondly, the ground-state absorption efficiencies of **4a** and **4b** are greater, if only marginally, than that of **1**, which might be expected to lead to superior lasing performance. Thirdly, the solubility of **4a** and **4b** in hexanes is significantly greater than for **1**, which permits higher concentrations of the lasing medium and mitigates complications of light scattering associated with the formation of micro-crystallites. Nonetheless, solutions of **4a** and **4b** do not lase. We believe that the reason for this is associated with excited state absorption (ESA) and the population of higher excited states. To investigate this hypothesis, we conducted an ultra-fast transient UV-vis absorption spectroscopic study of compounds **4a** and **4b**. The results are shown in Figure 13 and Figures S31-S33. The data for **4a** and **4b** are very similar to each other, and show two excited state absorption bands (one band at around 370-400 nm and a second band at around 500-520 nm) that both partially overlap with the stimulated emission (around 400-480 nm) from these compounds. The absence of negative absorbance values in Figure 13 confirms our initial hypothesis that stimulated emission from **4a** and **4b** is completely absorbed by the excited state and, as a consequence, lasing cannot occur.

Figure 13. Transient absorption spectra from solutions of compounds **1**, **4a** and **4b** in *n*-hexane. Excited at 340 nm.

A full analysis of the upper excited states photophysics and photochemistry of compound **1**, including the significance it bears on its laser properties, has recently been published²⁰ and several of its arguments are relevant here. ESA from **4a** and **4b** at the emission region between 400-480 nm strongly reduces the effective stimulated emission cross-section, and ESA close to the pump wavelength diminishes the pump to laser conversion efficiency, effectively raising the population inversion threshold of the system. The combination of these effects inhibits laser emission from **4a** and **4b**. However, it remains entirely possible that these limiting factors may be mitigated by the introduction of other substituents to the alkylated octadecaborane cluster. The exceptional emission properties of these species (quantum yields of unity and nanosecond lifetimes) mean that only partial success here would provide highly competitive blue-lasing materials.

Photophysical Calculations. Following from these experimental observations, a CASPT2 theoretical analysis of the photophysical properties of compounds **4a** and **4b** was carried out. CASPT2 – Complete-Active-Space Second-Order Perturbation Theory – is a multi-reference electron-correlation method for computational investigation of electronic states in a molecular system. Table 3 compiles the computed energies of the lowest-lying electronic states (the S_0 ground state, followed by the first four excited states, $S_1 - S_4$) as well as the oscillator strengths (f) associated with the $S_0 \rightarrow S_{1-4}$ absorptions at the $(S_0)_{\min}$ Franck-Condon geometry (ground state absorption) as a measure of the relative probability of each respective transition (values for **4b** are in given square brackets).

Table 3. Ground-state absorption spectroscopy ($S_0 \rightarrow S_X$) of **4a** and **4b** (in square brackets) computed with the CASPT2 method at the Franck-Condon geometry.

State	Absorption energy (eV)	λ (nm)	$f(S_0 \rightarrow S_X)$	Exp. Abs. λ (nm)
S₁	3.88 [3.78]	320 [328]	0.3547 [0.3557]	335 [337]
S₂	4.89 [4.73]	254 [262]	0.1098 [0.1301]	289 [290]
S₃	4.97 [4.86]	250 [255]	0.1997 [0.1718]	
S₄	5.73 [5.57]	216	0.0232	

Both $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ transitions are clearly visible in the measured ground state absorption spectra of both **4a** and **4b** (see Figure 10) and correlate well with the calculated data presented in Table 3. The principal transition for both **4a** and **4b** appears to be $S_0 \rightarrow S_1$, with associated oscillator strengths (f) of 0.3547 and 0.3557 respectively. These values are significantly greater than the value calculated for *anti*-B₁₈H₂₂ of 0.265,² which reflects the experimentally measured superior absorption of **4a** and **4b** over that for **1**.

Table 4 shows the calculated transient absorptions ($S_1 \rightarrow S_X$) for compounds **4a** and **4b** (again, values for **4b** are given in square brackets). A comparison of the calculated and measured data (Figure 13 and Table 4, far right column) shows good correlations, and reveals the photophysical behaviour of **4a** and **4b** once promoted to their S_1 excited states. In the case of **4a**, the most probable electronic transition is computed at 436 nm (−2.85 eV) with an oscillator strength of 0.2762 and corresponds to the $S_1 \rightarrow S_0$ emission, which is measured experimentally at 424 nm. However, competing with this emissive transition are three computed ESA transitions at 378 nm (3.28 eV), 496 nm (2.50 eV), and 752 nm (1.65 eV), the first two of which are readily assigned to the measured ESA bands with maxima at 375 nm and 510 nm (experimental data were collected up to 620 nm, therefore the third calculated ESA transition cannot be verified although the spectra do seem to be tending towards an increasing absorption at the 620 nm cut-off, seen in Figure 13). These ESA correspond to $S_1 \rightarrow S_{11}$ and $S_1 \rightarrow S_7$ and $S_1 \rightarrow S_6$ transitions with oscillator strengths of 0.1249 and 0.2398 and 0.0879, respectively, that are comparable to the magnitude of the oscillator strength for emission (see Figures S34 and S35 for visualizations of the electronic states of **4a** and **4b** responsible for these main ESA transitions).

Table 4. Excited-state absorptions ($S_1 \rightarrow S_X$) of **4a** and **4b** (in square brackets) computed with the CASPT2 method at the (S_1)_{min} geometry.

State	Rel. Energy to S_1 (eV)	λ (nm)	$f(S_1 \rightarrow S_X)$	Exp. Em. λ (nm)	Exp. Abs. λ (nm)
S₀	−2.85 [−2.74]	436 [452]	0.2762 [0.3104]	424 [427]	
S₁	0.00	-	-		
S₂	1.15 [1.19]	1075 [1043]	0.0081 [0.0000]		

S₃	1.23 [1.19]	1005 [1041]	0.0170 [0.0223]	
S₄	1.53 [1.40]	812 [886]	0.0110 [0.0000]	
S₅	1.63 [1.58]	761 [782]	0.0096 [0.0350]	
S₆	1.65 [1.62]	752 [766]	0.0879 [0.0579]	
S₇	2.50 [1.76]	496 [703]	0.2398 [0.0058]	~510
S₈	2.90 [2.37]	428 [524]	0.0217 [0.3092]	[~520]
S₉	3.08 [2.98]	403 [416]	0.0017 [0.0152]	
S₁₀	3.20 [3.09]	387 [401]	0.0506 [0.0000]	
S₁₁	3.28 [3.23]	378 [384]	0.1249 [0.0607]	~375
S₁₂	3.31 [3.27]	375 [380]	0.0239 [0.1588]	[~380]
S₁₃	3.50 [3.33]	355 [372]	0.0398 [0.0000]	
S₁₄	3.65 [3.64]	340 [341]	0.0193 [0.0000]	

Compound **4b** has very similar excited state photophysics, with ESA transitions computed at 380 nm (3.27 eV), 524 nm (2.37 eV), and 766 nm (1.62 eV) that approximate the measured ESA spectrum even more closely than for **4a**. These ESA transitions correspond to $S_1 \rightarrow S_{12}$, $S_1 \rightarrow S_8$ and $S_1 \rightarrow S_6$ transitions with oscillator strengths of 0.1588, 0.3092 and 0.0579.

Solid State Photophysics. Under exposure to a UV source, solid samples of the above alkyl derivatives are strongly luminescent (see Figure S36). Examination of the precise nature of this characteristic led to an unexpected finding in the case of compound **4b**. Thus, whereas solid-state samples of the tetramethyl derivative **4a** consistently give a single 430 nm blue luminescence over a range of excitation wavelengths up to 400 nm with a quantum yield of 0.39 (excited at 340 nm) (see Figure 14), the tetraethyl derivative **4b** displays two luminescence bands whose relative intensities strongly depend on the excitation wavelength; a stronger 435 nm blue band (quantum yield of 0.38 when excited at 340 nm) and a weaker 530 nm band predominant at excitation wavelengths above 400 nm (quantum yield of 0.09 when excited at 440 nm).

Figure 14. Emission spectra at various excitation wavelengths (340 nm – black; 400 nm – red; 440 nm – green) from solid-state samples of **4a** (left), **4b** (middle), and sublimed **4b** (right).

The contrasting solid-state luminescence of these two very similar compounds, differing only in the lengths of the alkyl substituents, that is not apparent in their photophysics in solution, suggests

explanation in their crystal structure supramolecular assembly. The multi-excitation and multi-emission phenomena observed for **4b** are associated with its tendency to crystallize from solution in two phases as suggested by the wavelength dependence of the relative intensities of the emission bands. By taking the same sample for which the multi-excitation and multi-emission data shown in Figure 14 were collected and subliming it, the resulting sublimate, present as just a single phase, exhibits only the single blue emission at 435 nm with a fluorescence quantum yield of 0.53 @340 nm (see Figure 14). A similar conversion to a single-emission property was also observed when the sample crystallized from solution was grinded with a pestle and mortar and dried in air, suggesting that the additional emission band at 530 nm originates from a borane-solvent interaction.

As a preliminary venture into optically active materials using the new fluorophores described here, polystyrene thin films of average measured thickness of 50 microns, containing 25 mM/l concentrations of the tetraethyl derivative **4b**, were prepared and studied. The photophysical data collected on these thin films are shown in Figure S36, and reveal properties very similar to solution behaviour of fluorophore **4b**. The colourlessness of the new fluorophores described herein, and the maintenance of the luminescent properties of compound **4b** in polystyrene thin films, bodes well for their potential use in optical devices. A sophisticated study of these, based on the fundamental structural and photophysical work described here would be a reasonable goal for future work.

Conclusions

This contribution is a comprehensive account of the synthesis, structural characterization and photophysical properties of a series of alkylated derivatives of *anti*-B₁₈H₂₂. All new compounds, which are also the first examples of alkylation of the macropolyhedral octadecaborane cluster **1**, are highly stable and demonstrate essentially 100 % efficiency in the conversion of UVA irradiation into blue light. All derivatives are therefore strongly luminescent in nanomolar concentrations, and the main products – the tetraalkylated species **4a** and **4b** – are available in yields (unoptimized ca. 15 % and 27 % respectively) sufficiently high to permit reasonable quantities for the routine fabrication of thin-film and solution-processed devices. The good number of derivatives isolated, ranging from two to thirteen substitutions, has permitted the analysis of trends in changes in molecular cluster volume and electron density with respect to the number of alkyl substitutions. We believe these considerations to be of value, in the light of the growing portfolio of luminescent derivatives of *anti*-B₁₈H₂₂, in the provision of important insights towards eventual molecular property design.

Experimental

General Procedures. Dried, deoxygenated solvents were stored over a suitable drying agent in evacuated flasks sealed with a high-vacuum Teflon stopcock. All other chemicals were purchased commercially and used as delivered. Reactions were carried out under an argon atmosphere using standard glove box and Schlenk-line techniques. Preparative thin-layer chromatography (TLC) was carried out using 1 mm layers of silica gel G (MN Silica Gel G/UV254) made from water slurries on glass plates of dimensions 20 × 20 cm and dried in air at 80 °C. Compound **1**, *anti*-B₁₈H₂₂, was prepared as described previously.²¹ NMR spectra were recorded on a JEOL 600 MHz (14.1 T) spectrometer, using ¹¹B, ¹¹B-{¹H} ¹H, ¹H-{¹¹B(broadband)}, ¹H-{¹¹B(selective)}, HSQC and HMQC techniques. DFT calculation of chemical shifts and geometrical parameters of ground state molecules were carried out using Gaussian 09¹⁴ at the B3LYP/6-31G(d) level. GIAO calculated ¹¹B shieldings²² were related to chemical shifts by comparison with the computed value for B₂H₆ which was taken to be δ(¹¹B) +16.6 ppm relative to the [F₃B(OEt₂)] = 0.0 ppm standard.

Methylated species. In a glove box, *anti*-B₁₈H₂₂ (504 mg, 2.31 mmol), AlCl₃ (1.0 g, 7.50 mmol) and methyl iodide (4 ml, 132 mmol) were placed in a round bottom flask, together with a magnetic follower. The flask was sealed (Young's vacuum tap), removed from the glove box, and stirred at ambient temperature for two weeks. The flask was opened to air and the contents washed out with hexane and HCl-acidified water into a flask containing HCl-acidified water. The mixture was extracted with hexane three times and the hexane solution dried with Na₂SO₄, filtered, and reduced to dryness on a rotary evaporator. The solid product was then dissolved in boiling hexane and allowed to cool in a refrigerator for *ca.* 1 h (4 °C). The obtained white solid was collected on a filter frit and washed with a minimum of cold pentane, affording 260 mg of product. The boron-11 NMR spectrum of the solid suggested that the main component, later identified as 3,3',4,4'-*anti*-B₁₈H₁₈ (**4a**), was present in *ca.* 80% yield. A number of consecutive crystallizations were required to obtain the compound free of other methylated components, ultimately yielding 86 mg, 0.32 mmol, 14% of material. The filtrates from the crystallizations were combined, reduced in volume and applied to preparative TLC plates with hexane as the mobile phase and affording five yellow bands R_F A 0.50, B 0.45 and C 0.30, D 0.20, E 0.10. Band B was identified as pure (**4a**). Band D was identified as 3,4,4'-Me₃-B₁₈H₁₉ (**3a**, 12 mg, 0.05 mmol, 2%). Band E was subjected to further TLC separation with 15% CH₂Cl₂/hexane giving a broad band at R_F 0.1 to the baseline which was removed from the plate as the top half and the bottom half was **3a** and the bottom half was identified as 4,4'-Me₂-B₁₈H₂₀ (**2**), 1 mg, 0.005 mmol, 0.17%). Band A, above, contained a mixture of the the pentamethylated compounds **5** and **6**, but these were subsequently isolated from a separate reaction using B₁₈H₂₂ (0.241 g, 1.1 mmol). AlCl₃ (0.35 g), MeI (4.0 ml). Here, in addition to the above compounds, two further minor components were isolated by preparative TCL of the filtrate remaining after crystallization of **4a**. At

the top of the plate a colourless band which fluoresced under UV irradiation (540 nm) was identified as 1,3,3',4,4'-Me₅-B₁₈H₁₇ (**5a**, 15 mg, 5 μmol, 5 %) and 3,3',4,4',8-Me₅-B₁₈H₁₇ (**5b**), 1.4 mg, 5 μmol, 0.5 %). Finally, it may be noted that two further very minor components were isolated. The first, present in all the preparations was 3,3',4-Me₃-B₁₈H₁₉ (**3b**). This would generally appear together with **3a** above, in the same TLC band, but at a much lower level of < 10% relative to **3b**. However, in one reaction it was produced in sufficient quantity to isolate and fully characterize as described in the text. The second, 1,1',3,3',4,4'-Me₆-*anti*-B₁₈H₁₆ (**6**), was isolated from the very top of the TLC plate in trace quantity and characterized by NMR spectroscopy and DFT calculation. Mass spectra for **2**, **3a**, **4a** and **5a** may be seen in Figures S37 to S40.

Additionally, it may be noted that similar mixtures when heated overnight in a water bath at 55 °C produces mixtures with methyl substituted compounds holding from 2 to 10 methyl groups but with the higher members containing iodine substituents. These were identified by high resolution mass spectrometry, Table 1.

3,3',4,4'-Et₄-*anti*-B₁₈H₁₈ (4b**).** In a glove box, *anti*-B₁₈H₂₂ (96 mg, 0.44 mmol), AlCl₃ (256 mg, 1.9 mmol) and ethyl iodide (5 ml, 165 mmol) were placed in a round bottom flask together with a magnetic follower. The flask was sealed (Young's vacuum tap), removed from the glove box, and stirred at ambient temperature for four days, after which time the contents were washed with hexane/water into a flask containing HCl-acidified water. The mixture was extracted with hexane three times and then the hexane solution was dried with Na₂SO₄, filtered and reduced to dryness on a rotary evaporator. The resulting solid product was then sublimed under vacuum (*ca.* 4 x 10⁻² mm Hg) at *ca.* 90 °C overnight onto a water-cooled finger. Next morning, 107 mg of material was removed from the cold finger. The title compound, 3,3',4,4'-Et₄-*anti*-B₁₈H₁₈, (21.3 mg, 0.065 mmol, 15%, m. pt. 138 °C) was obtained as a white crystalline solid by dissolving the sublimate in a minimal amount of pentane, heating to dissolve it, and leaving to cool in an insulating polystyrene block. The solvent was then cannulated with a Pasteur pipette and the solid washed with cold pentane. A second crystallization was required to obtain the pure compound. The high solubility of **4b** reduced the isolated yield, although the initial boron NMR spectrum of the sublimate on the cold finger showed that the title compound was present at up to 90%. M. Pt 128 °C. In another reaction, 54mg, 249 μmol, *anti*-B₁₈H₂₂, 0.16 g AlCl₃ and 3 ml EtI gave 20.2 mg, 61.4 μmol, 27% of product after hexane crystallization following extraction with hexane from the reaction mixture dissolved in dilute HCl. The hexane solution was reduced to a minimum volume and then left overnight in the freezer. The solvent was cannulated from the resultant crystals and these were washed with cold pentane which was also stored in the freezer (*ca.* -35 °C). The mass spectrum for **4b** may be seen in Figure S41.

Computational details. Unless otherwise stated, all optimizations for **4a** and **4b** have been carried out in *C_i* point group of symmetry. The ground (¹A_g) and first singlet excited (¹A_u) state equilibrium geometries were optimized with the complete-active-space self-consistent field (CASSCF) method

using an active space of 8 electrons in 8 molecular orbitals (MOs), in which four MOs are of A_u symmetry and the other four are of A_g symmetry. Single-point calculations were conducted on top of the obtained geometries using the state-average (SA)-CASSCF procedure with a larger active space, in particular, of 12 electrons distributed into 12 MOs, without imposing symmetry restraints. In order to compute the high-energy transitions summarised in Table 4 responsible for the transient absorptions at <355 nm, 15 and 20 roots were demanded in the SA-CASSCF procedure for **4a** and **4b**, respectively. The necessary dynamic electron correlation was included by means of the CASPT2 using the SA-CASSCF wave functions as a reference. An imaginary level shift of 0.2 au was used to avoid the presence of weakly intruder states, and the recommended ionization-potential electron-affinity (IPEA) parameter was set to the recommended value of 0.25 au, in coherence with recent works on related structures.^{5-7, 19, 23} All multiconfigurational calculations were performed with the OpenMolcas software package²⁴ and with the double- ζ basis set ANO-S-VDZP.

The HOMO-LUMO diagrams shown in Figures 11 and 12 correspond to the ground-state optimised structures in the gas phase of the compounds using the density functional theory (DFT) method, in particular of the B3LYP functional and the 6-31+G(d) basis set, as implemented in Gaussian 16.¹⁴ This level of theory was validated in previous works of very similar borane cages.^{3,6} In the case of **4a** and **4b**, the S_1 excited state was also optimised using time-dependent (TD)-DFT. No symmetry restrictions were imposed in neither the DFT nor TD-DFT optimizations.

DFT/GIAO nuclear-shielding predictions shown in Tables S1 to S5, the interatomic dimensions given in Tables S6 – S7, and those used in Figure 9, were performed using the Gaussian 09 package¹⁴ with the B3LYP/6-31G* methodology and basis set. This level is sufficient to give excellent correlation with the experimentally measured values. Calculated ^{11}B shielding values were related to chemical shifts by comparison with the computed value for B_2H_6 which was taken to be $\delta(^{11}\text{B}) + 16.6$ ppm relative to the $[\text{F}_3\text{B}(\text{OEt}_2)] = 0.0$ ppm standard.

Polystyrene film preparation and characterization: 2mL of chloroform solutions of 30 mg/mL polystyrene (PS) and 25 mM compound **4** were pipetted into a Petri dish 3 cm in diameter, covered by a larger Petri dish, and left to dry overnight under ambient conditions. Once evaporation of solvent was complete, the resulting thin-film membrane may be removed by the addition of water and physical displacement using tweezers to give homogenous thin films of approximately 44 microns in thickness at the center. These films were further dried in an oven at 70 °C for 20 minutes, and the membranes cut into the appropriate dimensions with a sharp blade. The absorption spectrum was obtained in a diode array spectrograph (Analytik Jena SPECORD 600) and the excitation and emission spectra were acquired in a spectrofluorimeter (HORIBA Jobin Yvon Fluoromax-4). The radiative life-time (τ_{rad}) was calculated from the absorption and emission spectra using the Strickler-Berg formula.²⁵

Transient absorption measurements: Prior to transient absorption measurements, the samples were diluted in *n*-hexane to a concentration of OD~1.7-2.0 at the pump wavelength (340 nm) in a 2 mm path length quartz cuvette. A magnetic stir bar, placed inside the cuvette, was rotated during the whole measurement to prevent/reduce photo-degradation. For generating excitation (pump) and probe pulses, a Spitfire Ace regenerative amplifier system (Spectra Physics), seeded with a Ti:sapphire oscillator (MaiTai SP, Spectra Physics), and pumped by a Nd:YLF laser (Empower 30, Spectra Physics), was used. The Spitfire Ace produces 100 fs pulses centred at 800 nm with a 1 kHz repetition rate. The output was divided into excitation and probe beams by a beam splitter. The excitation beam was transformed by an optical parametric amplifier (TOPAS Prime, Light Conversion, Lithuania) to a final wavelength of 340 nm. The probe pulses were generated by focusing the beam on a 3 mm CaF₂ plate, which was continuously moving. This setup allowed the generation of a white light continuum covering the 350-700 nm region. All the reflective optics which guided the white-light beam were covered by UV-enhanced aluminium to minimize losses in the UV region of the spectrum. To minimize chirp and chromatic aberration, the beam was collimated by an off-axis parabolic mirror and split by a broadband, 50/50 beam splitter to a reference and probe beam. The probe beam was focused by a 250 mm spherical mirror to the sample where it overlapped with the excitation beam. Probe and reference beams were focused to the entrance slit of a spectrograph and dispersed onto a pair of CCD arrays. The pump polarization was set at a magic angle (54.7°) relative to the probe polarization to eliminate any effects from rotational diffusion. The pump photon density at the sample was kept below 10¹⁴ photon cm⁻² pulse⁻¹. The transient absorption spectra were chirp corrected (software CarpetView, Light Conversion, Lithuania) by manually choosing the time zero for more than ten wavelength points and fitting it to a polynomial function.

X-ray crystallography

Single crystals of compound **2** and **3b** were obtained by vacuum sublimation in flame-sealed NMR tubes at 80 °C. Compound **3a** was obtained from a slow evaporation of a pentane solution, and **5b** and **11** from hot pentane solutions. In the latter case two crystal morphologies were evident; square plates, which correspond to compound **12**,¹² and needles of **11**. Compounds **4a** and **4b** were respectively obtained from hot hexane and slow dichloromethane evaporation. Crystal data, data collection, and refinement information are summarized in Table 5. Full details are given in the Supporting Information (Tables S8-S16). Crystallographic data were collected on a Rigaku/Oxford Diffraction Gemini A Ultra diffractometer using Cu K α radiation (λ = 1.54184 Å), except for compound **3b**, for which a set of data was also measured with synchrotron radiation (λ = 0.6889 Å) at beamline I19 of Diamond Light Source, using a custom-built diffractometer and a Pilatus 2M detector.^{26, 27} Structures were solved using SHELXT²⁸ and refined on all unique F^2 values with SHELXL.²⁹ All non-hydrogen atoms were refined using anisotropic displacement parameters; H atoms were treated by a mixture of

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3 free (B–H) and constrained riding (C–H) refinement. Two polymorphs were identified for compound
4 **3a**; the one reported here is ordered, while a second disordered form is included in the SI. Compound
5 **4a** was found to be twinned, with two components in the ratio 55.2:44.8(2) %. A set of synchrotron
6 diffraction data was obtained for a poor-quality crystal of compound **5a**; this was sufficient to confirm
7 the chemical identity and revealed an asymmetric unit containing one ordered molecule and one-half
8 of a disordered molecule lying on an inversion centre, but satisfactory refinement could not be
9 achieved. CCDC 2009105–2009112 contains the supplementary crystallographic data for this paper.
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Table 5. X-ray crystallographic collection and refinement data.

Compound No.	2	3a	3b	4a	4b	5b	11
CCDC	2009105	2009106	2009107	2009109	2009110	2009111	2009112
Formula	C ₂ H ₂₆ B ₁₈	C ₃ H ₂₈ B ₁₈	C ₃ H ₂₈ B ₁₈	C ₄ H ₃₀ B ₁₈	C ₈ H ₃₈ B ₁₈	C ₅ H ₃₂ B ₁₈	0.6C ₁₁ H ₄₂ B ₁₈ Cl ₂ · 0.4C ₁₂ H ₄₄ B ₁₈ Cl ₂
<i>M_r</i>	244.8	258.8	258.8	272.9	329.0	286.9	445.5
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / Å	10.8500(2)	6.1586(3)	6.1661(4)	7.0456(9)	7.7006(4)	7.2528(3)	15.7127(4)
<i>b</i> / Å	7.3128(2)	7.3565(4)	7.3673(5)	7.6241(7)	7.7616(4)	12.5466(3)	13.0207(2)
<i>c</i> / Å	10.7002(3)	19.7462(11)	10.0540(6)	9.3675(9)	9.3157(7)	10.8606(3)	13.0911(2)
α /°	90	95.959(5)	75.448(6)	74.690(9)	83.384(5)	90	90
β /°	109.258(3)	96.301(4)	87.914(5)	74.603(10)	75.819(5)	104.467(3)	92.9377(18)
γ /°	90	103.202(5)	76.707(6)	68.982(10)	77.804(4)	90	90
<i>Z</i>	2	2	1	1	1	2	4
μ mm ⁻¹	0.236	0.241	0.241	0.253	0.283	0.254	2.135
Measured reflections	10758	12099	6075	3050	7365	13224	19213
Unique reflections	1427	3029	1520	3050 ^a	1850	1694	4722
<i>R</i> _{int}	0.0371	0.0447	0.0241	0.0507	0.0281	0.0387	0.0403
Refined parameters	143	269	140	161	194	144	335
<i>R</i> (<i>F</i> ² > 2σ)	0.0384	0.0501	0.0427	0.0467	0.0405	0.0493	0.0396
<i>R</i> _w (all data)	0.1105	0.1486	0.1251	0.1366	0.1164	0.1431	0.1105
Goodness of fit	1.068	1.050	1.074	1.037	1.089	1.054	1.026
Max, min Δρ /e Å ⁻³	0.19, -0.14	0.27, -0.24	0.20, -0.14	0.23, -0.15	0.24, -0.14	0.20, -0.20	0.26, -0.23

^a Twinning prevents merging of equivalent reflections before refinement.

Associated content

Supporting information

The following data can be found in the supplementary information (SI) accompanying this manuscript: NMR Tables (Tables S1-S5); NMR Spectra (Figures S1-S28); Selected interatomic distances (Tables S6-S7); Calculated Natural Populations (Figure S29); Emission spectra (Figure S30); Transient Absorption Spectra and Kinetics (Figures S31-S33); Electronic states (Figures S34-S35); Solid-state emission and photophysics of polystyrene thin-films (Figure S36); Mass Spectra (Figures S37-S41); X-ray Crystal data (Tables S8-S16)

Conflicts of interests

There are no conflicts to declare.

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We present the first examples of alkylated derivatives of the macropolyhedral boron hydride, *anti*-B₁₈H₂₂. The new compounds are highly stable and convert UVA irradiation to blue light with fluorescence quantum yields of unity. We provide a broad perspective on their synthesis, molecular structures and photophysical properties, and highlight emerging patterns in the influence that

successive substitutions have on the molecular size of the 18-vertex borane cluster structure and distribution of electron density within.