

A molecular boron cluster-based chromophore with dual emission

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Bromination of the luminescent borane, *anti*-B₁₈H₂₂, via electrophilic substitution using AlCl₃ and Br₂ yields the monosubstituted derivative 4-Br-*anti*-B₁₈H₂₁ as an air-stable crystalline solid. In contrast to the unsubstituted parent compound, 4-Br-*anti*-B₁₈H₂₁ product possesses dual emission upon excitation with UV light and exhibits fluorescence at 410 nm and phosphorescence at 503 nm, with $\Phi_{\text{total}} = 0.07$ in oxygen-free cyclohexane. Increased oxygen content in cyclohexane solution quenches the phosphorescence signal. The fluorescent signal intensity remains unaffected by oxygen, suggesting that this molecule could be used as a ratiometric oxygen probe.

Introduction

Boron-containing luminescent molecules have been widely known and researched over decades for a variety of applications, including intracellular imaging,¹ sensors,² organic light emitting diodes³ photovoltaics,⁴ and lasers.⁵ While the properties of molecules such as triarylboranes and borate-based dyes have received considerable attention, research into luminescent boron-rich hydride-based materials remains an underexplored field in which *closododecaboranes*, also known as carboranes, have remained a central focus. This research has successfully developed emissive materials that incorporate carboranyl groups as components in metal complexes or luminescent polymers.^{3, 6} However, due to the large band gap of carboranes (~8 eV), substitution onto the icosahedral cage is usually required for the molecule to participate in visible light transitions.⁷ Consequently, a significant amount of work has focused on carborane functionalization methods.⁸ In fact, only one known polyhedral borane to date, *anti*-B₁₈H₂₂, possesses inherent luminescence. This unique cluster best resembles two *nido*-B₁₀H₁₄ molecules fused at two vertices, forming an 18-vertex borane (Figure 1). While two isomers of B₁₈H₂₂ are known- *anti*-B₁₈H₂₂ and *syn*-B₁₈H₂₂- only the former is luminescent, featuring intense blue fluorescence at 407 nm when irradiated at 340 nm that is accompanied by a high quantum yield of 0.97.⁹ Following its discovery in 1962,¹⁰ detailed analyses of its luminescence have been described,^{9,11} which found that both the HOMO and LUMO are distributed evenly across the boron cage. The absorbed energy in

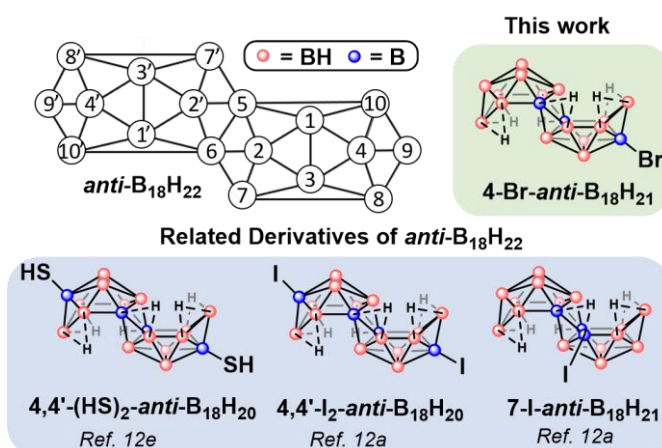


Figure 1: Top) Two-dimensional projection of *anti*-B₁₈H₂₂ and the brominated derivative discussed in this work. Bottom) Representations of select previously reported derivatives of *anti*-B₁₈H₂₂.

the S₁ state is redistributed across multiple bonds resulting in a prolonged S₁ lifetime and, consequently, fluorescence.^{9, 11} Since then, however, only a handful of synthetic derivatives of *anti*-B₁₈H₂₂ have been reported (Figure 1),¹² and a comprehensive synthetic foundation for this fascinating boron cluster system has yet to be established. From the existing reports it is clear that functionalization of the cluster dramatically alters its emissive properties.¹⁰ For example, thiolation of the cluster gives 4,4'-(HS)₂-*anti*-B₁₈H₂₀, which displays red-shifted luminescence with fluorescent emission at 536 nm and phosphorescent emission at 597 nm.^{12e} Reaction with pyridine yields a rearranged boron cage derivative, B₁₈H₂₀(NC₅H₅)₂, that exhibits thermochromic luminescence ranging from 585 nm (8 K) to 620 nm (300 K), which is caused by the constraint of the pyridine substituents at lower temperatures.¹³ Most recently, the iodination of this cluster was reported, which described the green phosphorescence of both 7-I-*anti*-B₁₈H₂₁ and 4,4'-I₂-*anti*-B₁₈H₂₀ at 525 nm and 545 nm, respectively.^{12a} Still, the relationship between B₁₈H₂₂ cluster structure and resulting photophysical properties has yet to be

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elucidated. It is therefore of great interest to explore functionalization methods and investigate the effect that such changes have on the photoluminescence profile. Following the first account of halogenated *anti*-B₁₈H₂₂, we were interested in how other halogens affect the luminescent properties of this cluster. Herein we report a synthesis for the first brominated derivative of *anti*-B₁₈H₂₂, 4-Br-*anti*-B₁₈H₂₁, and its unique photophysical characteristics distinctively different from the other halogenated analogues.

Results and Discussion

Synthesis and Structural Characterization of 4-Br-*anti*-B₁₈H₂₁

Following conventional electrophilic bromination protocols used previously with other polyhedral boron clusters,¹⁴ we treated *anti*-B₁₈H₂₂ with Br₂ (1 equiv) and AlCl₃ (10 mol%) in dichloromethane under an N₂ atmosphere at room temperature. Formation of the monobrominated cluster was observed after several hours, as suggested by an *in situ* mass spectrometry assay of the reaction mixture, although a significant amount of unreacted *anti*-B₁₈H₂₂ was still present after 18 hours. Increasing the amount of AlCl₃ (put the mol% here) resulted in higher conversion to B₁₈H₂₁Br with concomitant formation of the dihalogenated species, B₁₈H₂₀Br₂. Attempts to separate these two products were successful, but resulted in poor recovered yield of B₁₈H₂₁Br. Consequently, the procedure was further modified to improve the conversion to B₁₈H₂₁Br, which required fewer than 1 equiv of Br₂. These optimized conditions (15 mol% AlCl₃ and 0.70 equiv Br₂ in DCM) afforded a reaction mixture containing B₁₈H₂₂, B₁₈H₂₀Br₂, and B₁₈H₂₁Br as major products as judged by *in situ* mass spectrometry analysis. Subsequently, B₁₈H₂₁Br was purified from the crude mixture obtained from this reaction via high performance liquid chromatography (HPLC) using methanol/water mixture as an eluent on C-18 modified silica stationary phase.¹⁵ While the isolated material appeared pure by ¹¹B NMR spectroscopy, an impurity comprising ca. 5% of the bulk material was indicated by LC-MS

analysis. Consequently, further purification via HPLC was required to obtain >99% pure B₁₈H₂₁Br as determined by LC-MS (see Figure S6, Table S1). This product is stable when stored as a solid at 5 °C. This procedure was successfully reproduced several times to yield the same purity and photoluminescence profiles.

Single crystal X-ray diffraction analysis was used to determine the structure of 4-Br-*anti*-B₁₈H₂₁. Single, X-ray quality colorless crystals of 4-Br-*anti*-B₁₈H₂₁ were grown by dissolution of the compound in benzene followed by storage of the resulting solution at 5 °C (see SI). The solid-state structure of 4-Br-*anti*-B₁₈H₂₁ (Figure 2) indicates that the boron atom connectivity in the cluster remains the same compared to the parent molecule, and that the bromine atom is located on the 4 position of the octadecaborane cage. Prior analyses of *anti*-B₁₈H₂₂^{12a, 16} revealed that the 4 and 4' boron vertices are the most electron rich and therefore the most likely to undergo electrophilic substitution. Indeed, the doubly iodinated cluster, synthesized with I₂ and AlCl₃, is substituted at the 4 and 4' boron vertices.^{12a} Therefore, electrophilic substitution of bromide at these locations is expected under the given experimental conditions. Even so, it is worthy to note that bromide substitution on vertices other than 4 and 4' was not indicated by other analytical methods including ¹¹B NMR spectroscopy. The selectivity of electrophilic substitution may consequently be a helpful synthetic tool in the exploration of *anti*-B₁₈H₂₂ chemistry.

Photophysical Properties

The absorption spectra of 4-Br-*anti*-B₁₈H₂₁ and *anti*-B₁₈H₂₂ are shown in Figure 3. Both spectra display absorption within the ultraviolet (UV) range and the 4-Br-*anti*-B₁₈H₂₁Br absorbance spectrum displays minor peak changes compared to the absorption of *anti*-B₁₈H₂₂, shifting from 283 nm to 300 nm and 332 nm to 343 nm. However, the molar absorptivity for 4-Br-*anti*-B₁₈H₂₁ (ϵ_{342} =

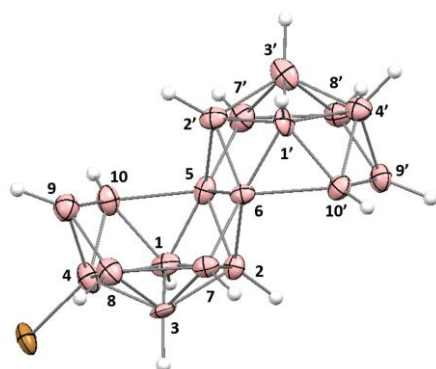


Figure 2: Single crystal X-ray structure of 4-Br-*anti*-B₁₈H₂₁•(2C₆H₆) with labeled boron vertices. For clarity, the bridging hydrides, benzene solvent molecules and cocrystallized impurities are not shown. Displacement ellipsoids are drawn at a 50% probability level.

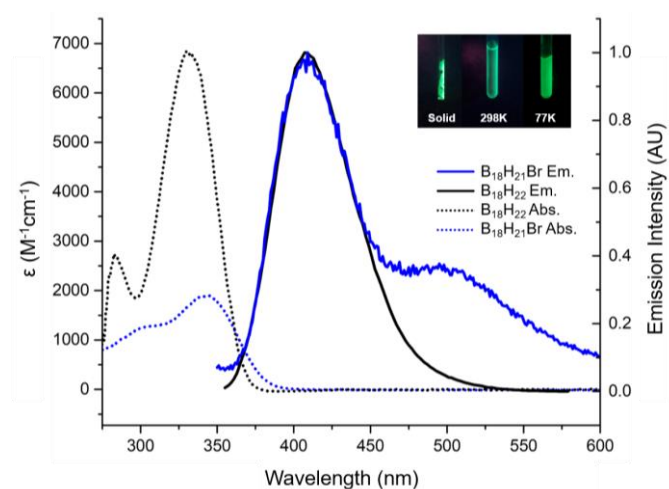


Figure 3: UV-vis spectra (dotted) of 4-Br-*anti*-B₁₈H₂₁ (blue, ϵ_{343} =1900 M⁻¹cm⁻¹) and *anti*-B₁₈H₂₂ (black, ϵ_{332} =6800 M⁻¹cm⁻¹). Emission spectra (solid) of 4-Br-*anti*-B₁₈H₂₁ (blue) and *anti*-B₁₈H₂₂ (black). The wavelengths of excitation are 350 nm and 340 nm, respectively. All measurements were conducted in cyclohexane solution. Inset: Luminescence of 4-Br-*anti*-B₁₈H₂₁ in the solid state at 298 K and in hexanes at 298 K and 77 K.

1900 M⁻¹cm⁻¹) is significantly lower than that of *anti*-B₁₈H₂₂ (ϵ_{332} = 6800 M⁻¹cm⁻¹).

Upon exposure to UV light, 4-Br-*anti*-B₁₈H₂₁ exhibits luminescence that is blue-green in hexanes solution at room temperature and green when the solution is cooled to 77 K. Likewise, this green luminescence persists in the solid state (Figure 3, inset). While *anti*-B₁₈H₂₂ is brightly fluorescent, we hypothesized that the bromide functionalized cluster would display some phosphorescent character due to the heavy atom effect.¹⁷ The attached bromine would presumably enhance spin-orbit coupling (SOC) and improve spin-forbidden intersystem crossing (ISC), which permits the population of triplet states that may undergo radiative decay to produce phosphorescence. To probe this possibility, photophysical data of 4-Br-*anti*-B₁₈H₂₁ were first obtained under ambient conditions in cyclohexane. While the UV-vis spectra of *anti*-B₁₈H₂₂ (λ_{max} 330 nm) and *anti*-B₁₈H₂₁Br (λ_{max} 340 nm) displayed in Figure 3 reveal slight differences in their λ_{max} values, the emission spectra exhibit more pronounced differences, with the brominated cluster displaying a shoulder at 503 nm. The variability in emission color, illustrated in Figure 3, prompted us to conduct more photoluminescence studies under various conditions. We suspected that the 503 nm shoulder observed could be phosphorescent in nature, but because room temperature phosphorescence is often difficult to observe the emission data were gathered at 77 K. Under these conditions, bimolecular and diffusional quenching processes are minimized and molecular motions are restricted due to the molecule existing within a solid glass matrix.¹⁸ With these pathways diminished, any occurring phosphorescence is likely to be detected. Indeed, at 77 K the 503 nm peak is intense, nearly obscuring the 410 nm signal (Figure 4). To investigate the possibility of oxygen-quenched phosphorescence, the photophysical data in degassed (O₂-free) cyclohexane were gathered at 298 K. The emission spectrum shows the 410 nm peak and a considerably more intense 503 nm signal (Figure 4), indicating that oxygen is at least partially responsible for the low peak intensity initially observed. The quantum yield (Φ) data, summarized in Table 1, also supports this hypothesis. Both cyclohexane solutions and PMMA films of 4-Br-*anti*-B₁₈H₂₁ possess smaller quantum yields when exposed to oxygen. The quantum yield of 4-Br-*anti*-B₁₈H₂₁ in cyclohexane under ambient conditions is 0.05, which increases to 0.07 when the measurement is conducted in oxygen-free solution. These low values are surprising considering that both iodinated clusters possess QY values no less than 0.41 in oxygen-free solution.^{12a} The contribution to QY from fluorescence and phosphorescence (Φ_{fluor} and Φ_{phos}) was also determined (see Figures S9 and S10). Under ambient conditions in cyclohexane, both $\Phi_{\text{fluor-amb}}$ and $\Phi_{\text{phos-amb}}$ are 0.025, while in oxygen-free solution Φ_{fluor} = 0.024 and Φ_{phos} = 0.046. Because the fluorescence quantum yield remains the same within error for both conditions, the decrease in quantum yield from 0.07 to 0.05 is most likely due to oxygen-quenched phosphorescence.

The quantum yield of a 4-Br-*anti*-B₁₈H₂₁ PMMA film was also assessed, increasing from <0.01 to 0.08 when under N₂, which is similar with the low values of the solid-state iodinated clusters (0.06 for 7-I-*anti*-B₁₈H₂₁ and 0.11 for 4,4'-I₂-*anti*-B₁₈H₂₀).^{12a} Because diffusion of oxygen at room temperature in PMMA is significantly slower than in cyclohexane, the system was allowed to equilibrate under the flow of O₂ for over 30 minutes (see Figure S8).¹⁹ Finally, the fluorescent and phosphorescent nature of these peaks were further explored through lifetime (τ) decay experiments. For a cyclohexane solution of 4-Br-*anti*-B₁₈H₂₁, the 410 nm peak lifetime is 10.6 ns under ambient conditions (Table 1, Figure S11), compared to that of the parent borane (11.2 ns).⁹ This value remains consistent under oxygen-free atmosphere (τ = 10.3 ns) and decreases slightly at 77 K (τ = 9.8 ns). The lifetime decay data was also gathered for the 503 nm peak, revealing a lifetime of 11.6 μ s in oxygen-free cyclohexane at 298 K. At 77 K, the lifetime is extended dramatically (τ = 552 μ s) (Table 1, Figure S11), which further supports the photoluminescence data in Figure 4. The photoluminescence, quantum yield, and lifetime data for 4-Br-*anti*-B₁₈H₂₁ under the conditions studied are summarized in Table 1. This data can be further contextualized through a comparison to the other reported monohalogenated derivative, 7-I-*anti*-B₁₈H₂₁.^{12a} The iodinated cluster contains only a single emission peak that is attributed to phosphorescence, which is probably due to the increased singlet and triplet state overlap that results from the heavy iodine atom.^{12a, 20} The monobrominated cluster displays attenuated ISC in comparison, achieving a balance between singlet and triplet states that permits dual fluorescent/phosphorescent emission.

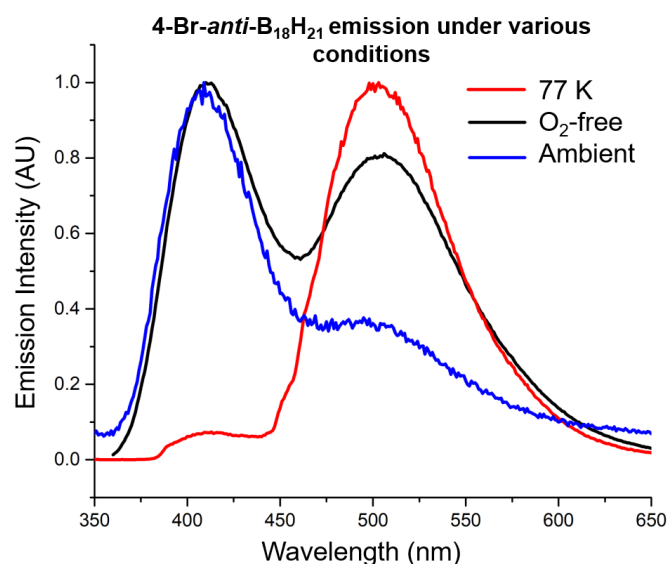


Figure 4: Emission spectra of 4-Br-*anti*-B₁₈H₂₁ in cyclohexane at 298 K under ambient conditions (blue), at 298 K in O₂-free cyclohexane (black), and at 77 K in methylcyclohexane (red). The wavelengths of excitation are 330 nm, 350 nm, and 340 nm, respectively.

4-Br- <i>anti</i> -B ₁₈ H ₂₁ Br	emission λ_{max}	Φ_{ambient}	$\Phi_{\text{O}_2\text{-free}}$	τ	$k_r 10^6 (\text{s}^{-1})$	$k_{\text{nr}} 10^6 (\text{s}^{-1})$
Cyclohexane O ₂ -free ^a	503	-	0.07 ^a	11.6 μs^{d}	0.0040 ^g	0.082 ^g
	410			10.3 ns ^e	2.3 ^h	95 ^h
Cyclohexane ^b	410	0.05 ^b	-	10.6 ns ^e	2.3 ^f	92 ^f
Methylcyclohexane ^c	503	-	-	552 μs^{d}	-	-
	407			9.8 ns ^e	-	-

Table 1 : Summary of photophysical properties of 4-Br-*anti*-B₁₈H₂₁. ^aCollected at 298 K under N₂ atmosphere. ^bCollected at 298 K under ambient conditions. ^cCollected at 77 K. ^dObtained by exciting at 372 nm and observing at 525 nm. ^eObtained by exciting at 331 nm and observing at 410 nm. Error in the excited state lifetime measurement is $\pm 14\%$ and $\pm 10\%$, respectively. ^{f,g,h}Calculated according to the equations $k_r = \Phi/\tau$ and $k_{\text{nr}} = (1 - \Phi)/\tau$, where k_r is the radiative rate constant, k_{nr} is the nonradiative rate constant, Φ is the quantum efficiency of fluorescence under ambient conditions ($\Phi_{\text{fluor-amb}}$), ^f of phosphorescence under N₂ (Φ_{phos}), ^g fluorescence under N₂ (Φ_{fluor})^h and τ is the excited state lifetime.

The simultaneous fluorescence and oxygen-sensitive phosphorescence demonstrated by 4-Br-*anti*-B₁₈H₂₁ is a property not commonly observed by small molecule metal-free emitters.²⁰ Although dual emission was reported for thiolated *anti*-B₁₈H₂₂, the two luminescence bands in this molecule overlap significantly, obscuring small changes in the oxygen-sensitive phosphorescence signal.^{10e} In contrast, the energy difference between the two emission events for 4-Br-*anti*-B₁₈H₂₁ is large enough that the fluctuating intensity of the phosphorescence peak is easily observed. These combined characteristics make the 4-Br-*anti*-B₁₈H₂₁ chromophore potentially useful for oxygen sensing. Emissive oxygen sensors have been intensely studied due to their wide applicability in biological imaging.²¹ Many dual-emitting sensors are nanoparticle or heavy-metal based, or require the combination of two different luminophores (one fluorescent, the other phosphorescent).²⁰ This is due to the difficulty involved in rationally designing a single dual-emitting small molecule with the appropriate balance of populated singlet and triplet states that would give rise to dual emission. This phenomenon is especially difficult to achieve with entirely organic systems, and most dual-emissive organic small molecules are based on polycyclic aromatic molecules such as pyrene²² or naphthalene.²³ However, each of these methods are accompanied by a host of disadvantages, such as unequal stability between mixed dyes, weak phosphorescence, photobleaching, and bio-incompatibility. The ideal ratiometric oxygen probe exhibits intense oxygen-sensitive phosphorescence, long lifetime, resistance to photobleaching, and stability.²⁰ To assess the applicability of 4-Br-*anti*-B₁₈H₂₁ as a small molecule oxygen sensor, preliminary sensing studies were conducted. Mixtures of nitrogen and oxygen gas containing varying amounts of oxygen were bubbled through a cyclohexane solution of 4-Br-*anti*-B₁₈H₂₁ before measurements were collected (see Table S4). As shown in Figure 5, phosphorescence decreases significantly with increasing oxygen content while the fluorescence peak maintains its intensity. This system functions as a ratiometric probe through comparison of the reference signal (the oxygen-insensitive fluorescence peak) to the intensity of the oxygen-quenchable phosphorescence peak. The intermolecular, collisional quenching process by oxygen follows Stern-Volmer kinetics (see Figure 6). Using a previously reported value for the solubility of oxygen in

cyclohexane²⁴ and the Stern-Volmer relationship, the Stern-Volmer quenching constant was calculated, $K_{\text{SV}} = 2200 \text{ M}^{-1}$ along with the bimolecular rate quenching constant, $k_{\text{O}_2} = 1.9 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$. The latter value can be directly compared to the quenching rate of 7-I-*anti*-B₁₈H₂₁ ($4.1 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) and 4,4'-I₂-*anti*-B₁₈H₂₀ ($6.8 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$).^{12a} It is evident that oxygen quenching occurs an order of magnitude faster in the brominated borane than its iodinated counterparts. Finally, the electrochemical properties of both *anti*-B₁₈H₂₂ and 4-Br-*anti*-B₁₈H₂₁ were assessed through cyclic voltammetry (see Figure S12). While both compounds exhibit an irreversible reduction, the reduction potential shifts cathodically from -1.36 V (*anti*-B₁₈H₂₂) to -1.18 V (4-Br-*anti*-B₁₈H₂₁). This difference of 0.18 V indicates that the brominated cluster is a stronger oxidant than its parent borane and could be a potent

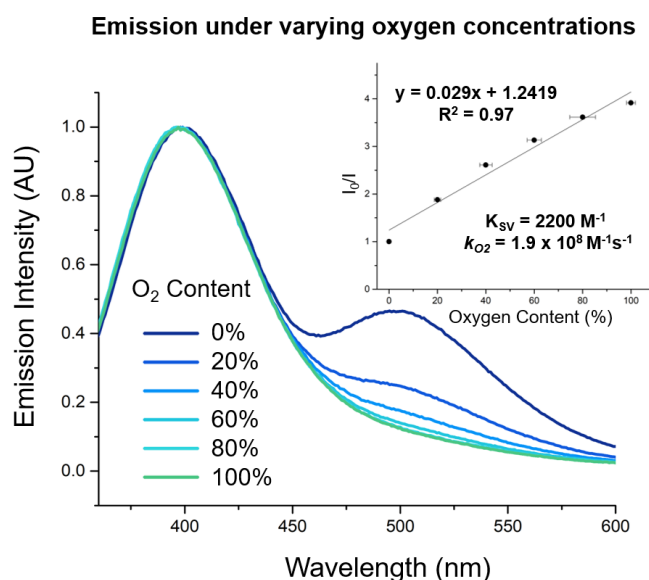


Figure 5: Emission spectra of 4-Br-*anti*-B₁₈H₂₁ in cyclohexane degassed with N₂ and O₂ gas mixtures containing varying amounts of oxygen. The wavelength of excitation was 320 nm. Inset) Stern-Volmer plot of phosphorescence quenching of the 503 nm peak. The quenching constant K_{SV} and bimolecular rate constant of T₁ state quenching k_q were calculated using 0.00116 mole fraction atm⁻¹ as the solubility of O₂ in cyclohexane²⁴ and the Stern-Volmer equation: $I^0/I = 1 + K_{\text{SV}}[\text{O}_2]$, $K_{\text{SV}} = k_{\text{O}_2}\tau_0$.

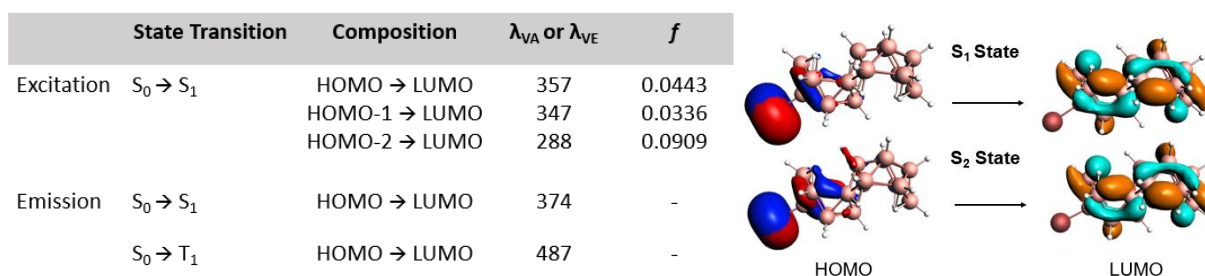


Figure 6: Left) Summary of relevant calculated absorption and emission spectra (Hybrid PBE0 DZP) for 4-Br-*anti*-B₁₈H₂₁, where λ_{VA} is the calculated vertical absorption wavelength, λ_{VE} is the calculated vertical emission wavelength, f is the oscillator strength, and λ_{max} is the corresponding experimental wavelength. Excitation calculations were based on the S_0 optimized geometry and emission calculations were based on the S_1 , S_2 or T_1 optimized geometries. Right) Natural Transition Orbitals (NTOs) for the electronic transitions of the S_1 and S_2 states. The remaining relevant NTOs are shown in Figure S14.

photooxidant.

DFT Analysis of Photophysical Data

As a supplement to experimental data, computational calculations were conducted using TD-DFT on ADF software. A DFT hybrid PBE0 functional and DZP basis set was used with scalar relativistic effects considered. Optimized geometry coordinates and frequency calculations can be found in Tables S6-9. First, the excitation spectrum was calculated based on the optimized singlet ground state geometry, S_0 . As shown in Figure 6, three vertical absorption (λ_{VA}) events with oscillator strengths > 0.02 occur between 290-350 nm, the approximate range in which the molecule was excited in the photoluminescence experiments. While these transitions originate from the HOMO (-8.31 eV), HOMO-1 (-8.42 eV), or HOMO-2 (-9.18 eV), they are all singlet-singlet processes that excite into the LUMO (-4.09 eV). Importantly, there are two calculated bands at 347 nm and 357 nm that correspond to the broad experimental band at 343 nm. The relatively small oscillator strengths for these transitions, which are ~ 3 -4 times smaller than those of *anti*-B₁₈H₂₂ (Table S5), are in accordance with the absorption spectrum and ϵ values in Figure 3. The emission spectrum, based on the optimized geometry of the S_1 state, was calculated, resulting in a vertical emission wavelength (λ_{VE}) at 374 nm, which best corresponds to the experimental λ_{max} at 410 nm. In order to determine the origin of phosphorescence, the T_1 optimized geometry was calculated. The energy difference between the S_1 and T_1 states is 0.22 eV, a relatively small gap in which intersystem crossing would be possible. Therefore, phosphorescence will most likely occur from the T_1 state. The emission spectrum based on the optimized geometry of the T_1 state was calculated, giving $\lambda_{VE} = 487$ nm, which can be assigned to the experimental band maximum $\lambda_{max} = 503$ nm. The natural transition orbitals (NTOs) for the S_1 , and S_2 states are highlighted in Figure 7, and the T_1 NTO, which is similar to the S_1 state, is included in Figure S14. These show that the HOMO for S_1 (-8.46 eV), S_2 (-8.44 eV), and T_1 (-8.68 eV) have predominantly bromine p-orbital (n_{Br}) character. Furthermore, the p-orbital for the S_2 state is orthogonal to the S_1 and T_1 excited states, which will consequently favor SOC and therefore ISC. This is consistent with the fast ISC process and TADF observed in the experimental lifetime decay experiments. All excited states transition into the LUMO (S_1 ,

S_2 , $T_1 = -4.09$, -4.20, -4.70 eV respectively), which is distributed exclusively on the boron cluster. While the parent borane exhibits a $^1(\sigma \rightarrow \sigma^*)$ transition involving B-B and B-H bonds (Figure S13), the 4-Br-*anti*-B₁₈H₂₁ can be characterized as $^1(n_{Br} \rightarrow \sigma^*)$ and $^3(n_{Br} \rightarrow \sigma^*)$ charge transfers.

Conclusions

This work presents the synthesis and photophysical characterization of the dually emissive *anti*-B₁₈H₂₁Br molecule, which was prepared from *anti*-B₁₈H₂₂ through electrophilic substitution with AlCl₃ and Br₂. This molecule is a rare example of a boron-based dual emitting chromophore. Its simultaneous fluorescence and phosphorescence originate from a delicate balance of S_1 and T_1 state population afforded by the bromide substituent. While the phosphorescence is quenched by oxygen, the fluorescence signal maintains its intensity, suggesting that this molecule could be useful as a ratiometric oxygen probe. More broadly, the synthesis of 4-Br-*anti*-B₁₈H₂₁ offers a contribution to the synthetic toolbox for *anti*-B₁₈H₂₂, while also elucidating the relationship between cluster structure and photophysical properties.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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