

TUNING THE PHOTOPHYSICAL PROPERTIES OF ANTI-B₁₈H₂₂ [1]

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Abstract:

The tuning of the photophysical properties of the highly fluorescent boron hydride cluster *anti*-B₁₈H₂₂ (**1**), by straight-forward chemical substitution to produce 4,4'-(HS)₂-*anti*-B₁₈H₂₀ (**2**), facilitates intersystem crossing from excited singlet states to a triplet manifold.^[1] This subsequently enhances O₂(¹Δ_g) singlet oxygen production from a quantum yield of Φ_Δ ~ 0.008 in **1** to 0.59 in **2**. This contribution describes the synthesis and full structural characterization of the new compound 4,4'-(HS)₂-*anti*-B₁₈H₂₀ (**2**) and uses UV-vis spectroscopy coupled with DFT and *ab initio* computational studies to delineate and explain its photophysical properties. Additionally, we will report on new fluorescent derivatives of *anti*-B₁₈H₂₂ and their immobilisation on solid nanostructured substrates.

Key words:

boran hydrides, singlet oxygen, fluorescent boranes

1. INTRODUCTION

Although some pyridine derivatives of other cluster boranes and carboranes have been reported to be luminescent under UV irradiation, the high quantum yield fluorescence (Φ_F = 0.97) seen for *anti*-B₁₈H₂₂ is unique among the neutral binary boron hydrides.^[2] In addition to fluorescence, the production of O₂(¹Δ_g) singlet oxygen via an energy transfer process from a lowly populated triplet manifold (Φ_Δ = 0.008 in hexane solutions) was also observed.^[2] Density Functional Theory (DFT) and *ab initio* calculated Potential Energy Hypersurface (PEH) minima and crossings for *anti*-B₁₈H₂₂ showed that all its triplet states lie, in terms of their relative energies, far from the S₁ state minimum, thus making intersystem crossing (ISC) to triplet states highly unlikely at this point (see Figure 1).

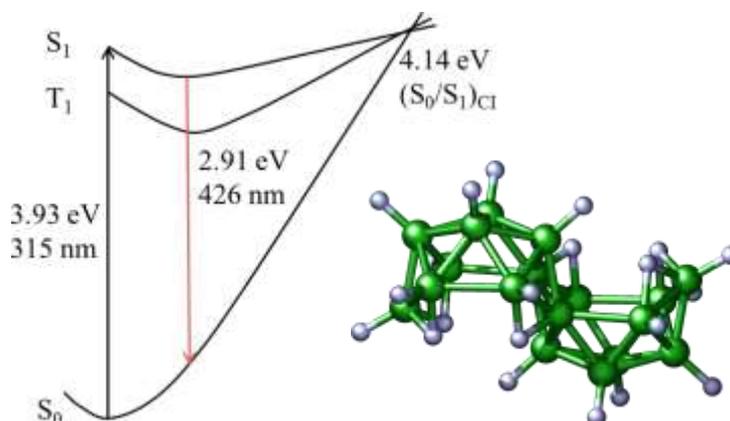


Figure 1. DFT and *ab initio* calculated PEH minima and crossings for *anti*-B₁₈H₂₂. (See reference 2 for full calculational and experimental)

This finding is significant as S_1 state minimum structures are usually the most favorable for ISC as energy is trapped there for a sufficient time for such processes to occur. This is not the case for the *anti*- $B_{18}H_{22}$ system, which, instead, sees the S_1 - T_1 energy gap decreasing as it approaches the (S_0/S_1) conical intersection point along the PEH surface (see Figure 1), making this point the most likely for ISC to occur. That the (S_0/S_1) conical intersection crossing is so high in energy relative to the S_1 state minimum is, essentially, the reason that *anti*- $B_{18}H_{22}$ overwhelmingly favors fluorescence rather than ISC and the subsequent formation of $O_2(^1\Delta_g)$ singlet oxygen.^[2] However, these observations do evoke the question: **Could the latter S_1 - T_1 quantum hop be facilitated, and the molecule induced into producing singlet oxygen more efficiently?**

2. RESULTS AND DISCUSSION

2.1. Synthesis and Structural Characterization of 4,4'-(HS)₂-*anti*- $B_{18}H_{20}$

Our previous computational study on the photophysics of *anti*- $B_{18}H_{22}$ indicates that the additional energy this molecule receives after irradiation is distributed over a number of molecular vibrational modes, or interboron connectivities, as it moves along the PEH from its S_1 minimum toward the (S_0/S_1) conical intersection point (see Figure 2).

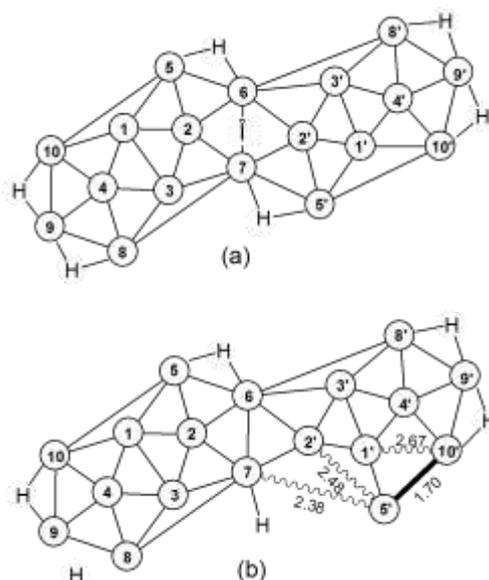


Figure 2. (a) *anti*- $B_{18}H_{22}$ molecular geometry at S_0 ground state, C_i symmetry. (b) *anti*- $B_{18}H_{22}$ molecular geometry at (S_0/S_1)CI. (wavy lines indicate connectivity elongation; thick lines indicate contraction).

The molecular geometry of the $\{B_{18}H_{22}\}$ cluster at the (S_0/S_1)_{CI} point guided our thinking when considering what chemical change might maximize the probability of ISC between S_1 and T_1 states, that is, a molecular modification in which the eighteen vertex geometry would be essentially preserved. A survey of the literature, however, revealed that the great majority of known derivatives of *anti*- $B_{18}H_{22}$ have significant alterations in the overall cluster molecular geometry, and are very often with additional or fewer vertices. Accordingly, we chose to take advantage of a well-recognized synthetic procedure that has been used with several other boron hydride species while producing only small changes in their molecular geometries, namely, cluster thiolation.

Thus, the heating of *anti*- $B_{18}H_{22}$ with a 10-fold excess of elemental sulfur and $AlCl_3$ in a sealed glass tube gave the new compound 4,4'-(HS)₂-*anti*- $B_{18}H_{20}$ in yields of up to 80%. Figure 3 shows the molecular structure of the resultant benzene solvate of 4,4'-(HS)₂-*anti*- $B_{18}H_{20}$.

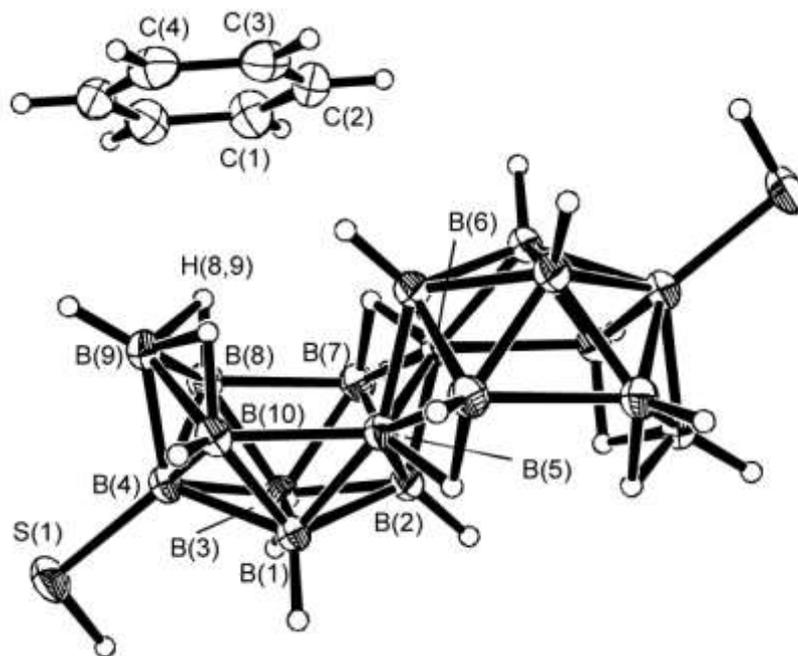


Figure 3. Crystallographically determined molecular structure of the benzene cocrystallite of 4,4'-(HS)₂-*anti*-B₁₈H₂₀.

2. 2. Photophysics of 4,4'-(HS)₂-*anti*-B₁₈H₂₀

Our photophysical study of new 4,4'-(HS)₂-*anti*-B₁₈H₂₀ (see Figure 4) found that initial excitation results in promotion to the S₃ state followed by decay to the S₁ through vibrational relaxation and internal conversion within a femtosecond time scale. Once the system reaches the S₁ energy minimum two possible outcomes dominate...

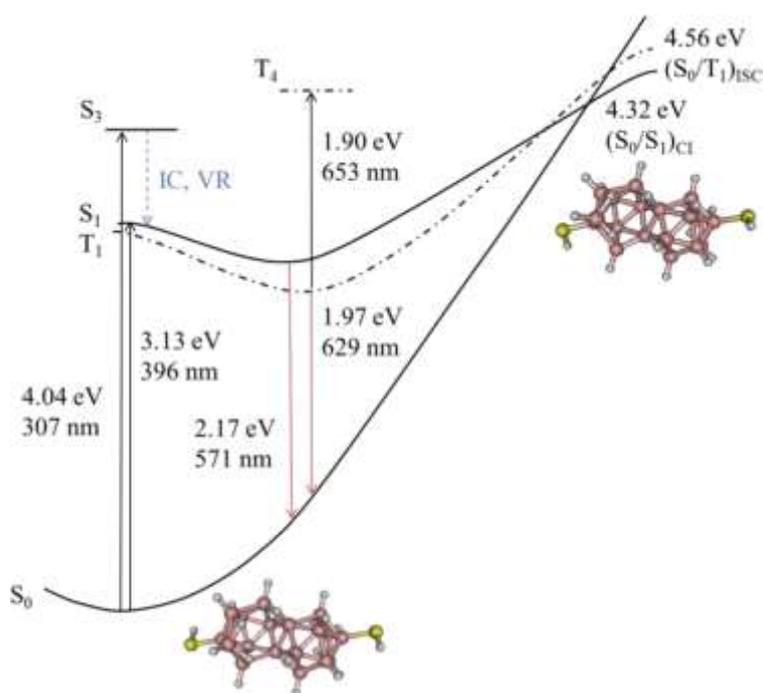


Figure 4. Photophysics and Potential Energy Hypersurface (PEH) of 4,4'-(HS)₂-*anti*-B₁₈H₂₀.

...The first of these is intersystem crossing (ISC) to, and population of, a triplet manifold (T_1), which is possible (and, indeed, likely) because the energy difference between S_1 and T_1 is a relatively small 0.14 eV, with a computed SOC of 3.37 cm^{-1} . The second most possible outcome is a fluorescence emission, computed at 571 nm (2.17 eV) and measured experimentally at 536 nm (2.31 eV).

This fluorescence was measured experimentally to have a relatively short lifetime (0.94 ns), which indicates competition between fluorescent and non-radiative processes such as ISC to populate the lowest-energy triplet manifold.

The formation of the triplet states has been monitored experimentally by transient absorption and time-resolved phosphorescence. These long-lived transients can be attributed to triplet states because they are quenched effectively by oxygen to generate singlet oxygen. The quantum yield of the singlet oxygen formation, Φ_Δ , for 4,4'-(HS)₂-*anti*-B₁₈H₂₀ in an air-saturated cyclohexane solution, is 0.59.

3. CONCLUSIONS

We have demonstrated that the tuning of the fluorescent *anti*-B₁₈H₂₂ cluster, by straightforward chemical substitution to produce 4,4'-(HS)₂-*anti*-B₁₈H₂₀, facilitates ISC from excited singlet states to a triplet manifold. This subsequently enhances singlet oxygen production from a quantum yield of $\Phi_\Delta \sim 0.008$ to 0.59, which is a value comparable to those of typical sensitizers such as porphyrins and phthalocyanines.

The luminescence of 4,4'-(HS)₂-*anti*-B₁₈H₂₀ together with its ability to generate O₂(¹Δ_g) is a significant and exciting combination of properties that warrants a greater degree of investigation. Consequently, we are currently focusing our efforts on the investigation of the potential applications of these properties.

ACKNOWLEDGEMENT

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[1] Sauri V., Braborec J., Londesborough MGS., et al. *Inorg. Chem.*, 2013, **52**, 9266-9274

[2] Londesborough MGS., et. al. *Inorg. Chem.*, 2012, **51**, 1471-1479