FROM BORANE CLUSTER TO BLUE LASER: UNDERSTANDING AND CONTROLLING THE PHOTOPHYSICS OF ANTI-$B_{18}H_{22}$

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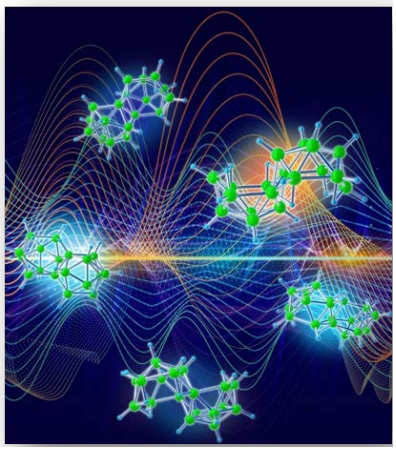

Fig. 1. *The fascinating Photophysics of anti-$B_{18}H_{22}$*

Abstract

Boranes are traditionally associated with unusual structures and electron-deficient bonding, but their potential as functional optical materials remained largely unexplored until the photophysical properties of the macropolyhedral cluster *anti*-$B_{18}H_{22}$ were established [1]. Under pulsed excitation, solutions of this intensely fluorescent and photostable compound generate blue laser emission centred at 406 nm with an energy-conversion efficiency of up to 9.5% [2]. This result identified *anti*-$B_{18}H_{22}$ as the first borane-based laser gain material and opened a new area of molecular laser chemistry.

This presentation traces the development of the borane laser and the subsequent experimental and theoretical work undertaken to understand its performance. Comparison with weakly emissive *syn*-$B_{18}H_{22}$ demonstrated the decisive influence of cluster architecture on excited-state relaxation [1]. Later studies revealed a more complex excited-state landscape in which non-radiative decay, intersystem crossing, triplet-state formation, excited-state absorption, concentration effects and higher-lying electronic states compete with stimulated emission [3]. Their relative importance varies with excitation wavelength, pulse duration, solvent, concentration and resonator conditions. Thus, high fluorescence yield and photostability are necessary, but not by themselves sufficient, for optimum optical gain.

The B_{18} framework is also a chemically addressable three-dimensional fluorophore. Substitution with sulphur, iodine or nitrogen-donor groups can change absorption and emission energies, fluorescence lifetimes and the balance between singlet and triplet states; iodination, for example, redirects the excited-state population towards efficient oxygen photosensitisation [4]. Particularly significant was the preparation of the first alkylated *anti*-$B_{18}H_{22}$ derivatives. Replacing selected terminal B–H groups with B–C bonds modifies the electronic distribution while retaining blue emission. Several alkylated clusters display stronger absorption and fluorescence quantum yields approaching unity, and one provided a second borane-based laser gain medium [5]. Extensive methylation also revealed a measurable expansion, or ‘swelling’, of the borane framework, linking substitution, charge distribution and cluster geometry [6]. Together, these results show that *anti*-$B_{18}H_{22}$ is not merely a fluorescent curiosity, but a tuneable inorganic platform for designing laser and photonic materials with controllable excited-state behaviour [7].

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