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Computational Design of Hybrid Polyoxometalate Structures for Advanced Chemical Catalysis

In today's world, the quest for green alternatives has become paramount across industrial sectors such as chemicals, textile, pharmaceutical and agriculture because they are facing a persistent challenge with increasing energy consumption during operation of their chemical reactions. In this regard, polyoxometalates (POMs), metal oxide clusters composed of early transition metals in high oxidation states like V^{5+}, Mo6+, and W6+, have gained attention as photocatalysts offering a clean, efficient, and environmentally friendly alternative to energy-intensive processes. However, most POMs exhibit absorption of solar energy in the UV/near visible-light region, which comprises only ˜5% solar light. The primary goal of this project is to investigate the photochemical mechanism of non-hybrid and hybrid POMs to underpin development of hybrid polyoxometalate structures for advanced chemical catalysis.

DFT and TDDFT have been used to explore the photocatalytic behaviour of the widely used tetrabutylammonium decatungstate (TBADT) catalyst. Geometries of the ground and valence excited states (S_0, S_1, T_1–T4) were optimised, along with the inter-system crossing (ISC) geometry between the lowest allowed singlet state and the doubly-degenerate triplet state, and spin-orbit coupling (SOC) constants. Three different basis set / ECP combinations (SRSC, CRENBL and Def2) and five different density functionals (BP86, B97x-D3, B3LYP, CAMB3LYP and LRCPBE) were compared to identify the optimal basis set and functional combinations. The singlet and triplet states involved in the ISC process were identified. The optimized geometries of the oxidised [W_10 O_32]ˆ(4-)and reduced [W_10 O_32]ˆ(5-) forms were used to calculate the reduction potentials and it was compared to experimental CV data. Ongoing further calculations to model the electronic structure and related properties of the TBADT photocatalyst are expected to yield deeper insights into its reactivity and catalytic performance.

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