Employing Density Matrix Renormalization Group (DMRG) Methods to Explore Nickel-based Photoredox Catalysts

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The ability of transition metal catalysts, induced by excitation by visible light, to serve as platforms for forging carbon-carbon and carbon-heteroatom bonds has spurred the extensive growth of metal-based photoredox catalysis in organic synthesis.[1] These pathways have bio-relevant applications, such as in synthesizing bioactive compounds, agrochemicals, and pharmaceuticals. [2,3] Nickel-based catalysts have emerged as a particularly promising metallophotoredox catalyst due to their ability to easily undergo one-electron oxidation state changes. [4]

Computational studies have been particularly useful in exploring nickel-based catalysts, with density functional theory (DFT), which uses electron density to describe electronic structures, being one of the most popular methods. While DFT is computationally efficient, the single-determinantal nature of DFT makes it inaccurate for multi-configurational (MC) systems, like transition metal systems. Experimental studies have demonstrated the significant MC character of catalytic nickel complexes.[5,6] Thus, in the case of catalytic nickel complexes, multiconfigurational methods are much better suited to describe their energetic characteristics.

To provide a starting point for multireference calculations, we used DFT methods to optimize the ground state molecular geometry of Ni(bpy)ArCl. The Pipek-Mezey (PM) method, which maximizes the charges of each orbital, was used to localize molecular orbitals.[7–9]

Multiconfigurational complete active space (CAS) calculations were performed on DFT-optimized geometries with an active space of 10 electrons in 9 orbitals active space. We did complete active space self-consistent field (CASSCF), complete active space second order perturbation theory (CASPT2), and complete active space pair density (CASPDFT) calculations for the first 5 energy roots. CASSCF includes all possible configurations of specified orbitals, which make up the active space, while CASPT2 and CASPDFT incorporate further electron correlation. However, while CASSCF, CASPT2, and CASPDFT can be effective for moderately sized systems, the number of determinants required to perform a calculation scale exponentially, leading to high computational costs. In addition, there is a limit to the active space in terms of size for CAS, meaning that CAS methods fail to successfully describe large systems, such as the nickel catalyst system.[10] These CAS calculations we ran will serve as points of comparison for further MC calculations, namely density matrix renormalization group (DMRG) calculations, that incorporate larger active spaces.

We employed DMRG methods with the same active space of 10 electrons in 9 molecular orbitals to verify DMRG methods as accurate. After confirming the accuracy of DMRG, we completed an expanded active space DMRG calculation with 24 electrons and 28 molecular orbitals.

Our expanded active space DMRG calculation demonstrated the ground state of Ni(bpy)ArCl as moderately multiconfigurational and all excited states as highly multiconfigurational. Furthermore, the energy levels of the d-orbital splitting in Ni(bpy)ArCl was, in order from lowest to highest, $d_{x^2-y^2}$, d_{xy}, d_{xz}, d_{yz}, and d_{z^2}, which differs from a perfect square planar geometry. We plan to conduct a 15 energy state calculation using DMRG to further investigate the ground state character and d-orbital splitting.

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