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Computational Study of Catalytic Enantioselective Visible-Light-Mediated 6π-Photoelectrocyclization

Computational Study of Catalytic Enantioselective Visible-Light-Mediated 6π-Photoelectrocyclization

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Photocatalyzed reactions are an excellent technique to generate chiral compounds. When combined with Lewis acid ligands, these processes can be driven by visible light, making them more economically viable and environmentally friendly. This work aims to investigate the mechanisms and origins of enantioselectivity in the catalytic, enantioselective, visible-light-mediated of aryloxyhexenones [1-2] by developing a computational model capable of rationalizing the experimental findings.

The theoretical investigation is structured into five major areas: (i) photosensitizer excitation, (ii) energy transfer, (iii) formation of metal–chiral ligand–substrate complexes, (iv) absorption spectra of complexes, and (v) elucidation of reaction mechanisms. A general scheme is presented in Figure 1.

Figure 1: General mechanistic framework of the studied reaction. M = metal center, PS = photosensitizer. Blue lamp indicates visible-light irradiation.

The structures were optimized with Def-TZVPP/PWPB95//Def2-SVP/wB97X-D3BJ DFT methodology. TDDFT calculations identified significant bathochromic shifts in copper and tin complexes, facilitating visible-light absorption. Mechanistic studies uncovered that ring-closure is the stereochemistry-determining step. N-Oxide ligands displayed a high isomeric ratio for the complexation step. For the copper(II)-bisoxazoline complex, chiral induction significantly raised the energy barrier for disfavored enantiomers ($\Delta\Delta G‡$ = 12.5 kcal/mol), highlighting the potential for high enantioselectivity. Multireference CASSCF/CASPT2 calculations confirmed an intramolecular charge-transfer character in the excitation, but with near zero force oscillator for all excitations.

Future work will explore dynamic excited-state processes using SHARC simulations and extend experimental validation to Ir-based photosensitizers and modified ligands. This integrated approach advances the rational development of enantioselective photochemical reactions under mild conditions.

[1] V. Edtmüller, et al., Tetrahedron, 2017, 73, 5038–5047 [2] M.D. Smith et al., Angewandte Chemie International Edition, 2017, 56, 468-9472

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