Computational Discovery and Mechanistic Investigations on Transition Metal Complex and Organic Mechanophores and Mechanophore-Enhanced Polymers

By

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Polymers are indispensable cornerstones for modern world, yet their production and disposal are bringing significant environmental impacts. To address this challenge, mechanophores have been developed to enhance the mechanical properties and lifetimes of polymers. However, as current mechanophore research focuses on organic molecules with few specific base motifs and rely mainly on time-consuming experimental validations, new mechanophore discovery have gradually plateaued, and critical limitations with currently developed mechanophores remain unaddressed. Transition metal complexes represent a vast, promising, yet underexplored design space of mechanophores. Moreover, various computational methods have been developed over the past two decades to accurately model the behaviors of molecular units under applied force. These methods can be further combined with machine learning or LLM models to accelerate mechanophore and material design.

Consequently, this thesis advances the computational discovery of novel transition metal and organic mechanophores First, I adopted computational screening to discover synthetically accessible Fe(II) and Co(II) spin-crossover mechanophores that exhibit force-activated magnetism, enabling potential force sensing in opaque engineering polymers. Analysis of spin-state energetics and coordination bond lengths revealed general design principles for predicting mechanically induced spin crossover and prioritizing highly responsive, robust candidates. Next, I developed a virtual screening workflow for Cu(II) conformation-switching mechanophores, identifying candidates with low activation forces, intrinsic reversibility, and self-repairing behavior. Chemical principle analysis and machine-learning models further clarified how metal–ligand coordination and ligand strain govern mechanochemical reactivity. Moreover, I further investigated the mechanism behind superior polymer reinforcement by Cu(II)-MeBip and the relationship between spin state and reactivity in Fe(II)-MeBip mechanophore, further reinforcing my findings on Cu(II) conformation-switching and Fe(II) spin-crossover mechanophores.

Beyond transition-metal systems, I also used *ab initio* modeling to establish molecular-level mechanisms for organic mechanophores relevant to drug delivery, phototherapy, and polymer enhancement. In Chapter 5, I elucidated the two-step C–C bond scission and cargo-release mechanism of SO_2-releasing 8-thiabicyclo[3.2.1]octane 8,8-dioxide (TBO) mechanophores and explained the enhanced reactivity of the *endo*-TBO stereoisomer. In Chapter 6, I investigated the CO-releasing, aggregation-induced emission NEO mechanophores, revealing how functional group substitution and aggregation-modified excited states affect emission wavelength and fluorescence behavior. Finally, in Chapter 7, I constructed a large-scale database of experimentally synthesized hydrogels and their mechanical properties using an accurate and efficient LLM-based text-mining pipeline. This database act can facilitate the design of mechanophore-enhanced hydrogels compatible with key applications. Together, my studies establish a computational framework that integrates high-throughput screening, mechanistic analysis, molecular modeling, machine learning, and literature data extraction to accelerate the design of mechanophore-containing polymer materials with enhanced mechanical strength and various applications.