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Electron coupling and electron transfer between two bridged dimolybdenum units

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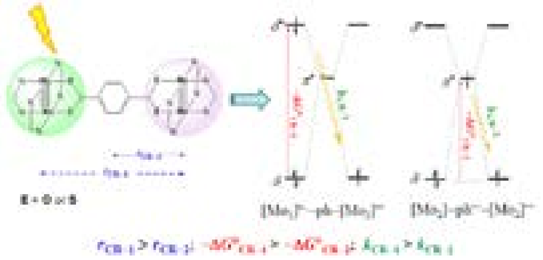
Bridged dimolybdenum dimers, denoted as [Mo_2]-bridge-[Mo_2], are favorable model compounds for study of electronic coupling and electron transfer because of the unique electronic structure of the [Mo_2] unit. The formation of the metal-metal multiple bond removes the d orbital degeneracy, rendering the Mo_2 unit a $\sigma^2\pi^4\delta^2$ electronic configuration. Therefore, as an electronic donor-bridge-acceptor system, the transferring electron is specified to be the δ electrons and donor-acceptor electron transfer can be probed by the metal (δ) to bridging ligand (π*) and bridging ligand (π) to metal (δ) and vibronic (δ) metal to metal (δ) charge transfer absorptions in accordance with sup exchange theory. By varying the ancillary ligands and the bridging ligands, a diverse of complexes of this type have been synthesized and studied. The electronic coupling matrix elements (H) are evaluated according to the Mulliken-Hush and CNS theories, which give consistent results. The mixed-valence properties are discussed in terms of Robin-Day's scheme. System transition from Class II to Class III via Class II-III is examined in a series of four complexes with subtle structural differences. The δ→δ electron transfer kinetics in symmetrical as well as asymmetrical systems has been investigated, conforming well to the semi-classical two-state model and the Marcus-Hush theory. In study of the photo-induced electron transfer, we found the δ*→δ back electron transfer is faster than the process from the bridge to the Mo_2 center by one order of magnitude, while in the latter case, the electron transfer distance is shorter but the electronic coupling is much stronger. This controversial electron transfer phenomenon is tentatively attributed to a quantum incoherent pathway.



Biography

Chun Y Liu completed his PhD in 2005 at Texas A&M University. Currently, he is a Full Professor at Jinan University. His research has been focused on study of electronic coupling (EC) and electron transfer (ET) between two charge bearing sites by taking a molecular approach. He uses quadruply bonded Mo-Mo complex units as the electron donor (D) and acceptor (A) and a diverse of organic bridging ligand (B) to construct D-B-A experimental models, in which the transferring electron is identified to be the δ electrons. Quantitative evaluations of the EC and ET properties are achieved with the physical chemical parameters (Hab, ΔG°, ΔG*, λ, Ket…) derived from electrochemical and spectroscopic data under the semi-classical theories. In study of photo-induced electron transfer, it is found that the δ*→δ back electron transfer is quite different from the δ→δ ET reaction in the mixed-valence systems, thus, a quantum incoherent pathway is proposed.

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