

Insights into Photochemical Synthesis and Photoluminescence Mechanisms of Tungsten Complexes for Advanced Material Applications

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Transition-metal complexes (TMCs) are pivotal in optoelectronics, solar energy conversion, and biomedical applications. Our study provides two complementary approaches to shed light on the (a) photochemical synthesis pathways and (b) photoluminescence (PL) mechanisms in these complexes. For photochemical synthesis, we combine time-dependent excited-state molecular dynamics (TDESMD)^{1,2}, informed by Rabi oscillations, with a time-dependent density matrix approach, to reveal the intricacies of ligand exchange reactions and excited-state reaction processes. Our results highlight the pivotal role of ligand-to-metal charge transfer (LMCT) in facilitating W-C bond dissociation, leading to the formation of reactive intermediates and the progression from $W(CO)_6$ to $W(bpy)(CO)_4$ complexes. This method study allows us to explore the pathways of photoactivated reaction dynamics and assess the intermediates formed during the reaction and the transition states along this path. Concurrently, for characterization of these complexes, we explore the PL behavior through the Reduced Density Matrix equation of motion, uncovering the dominant role of electronic energy dissipation into nuclear degrees of freedom, relaxation dynamics, and nonradiative recombination. These explorations connect electronic relaxation to PL spectra. The $W(bpy)(CO)_4$ complexes demonstrate substantial quantum yield improvement, exhibiting notable infrared emissions compared to $W(CO)_6$ complexes with minimal UV and no IR emissions. The IR emission from $W(bpy)(CO)_4$ complexes highlights the significance of both MLCT and LMCT processes, electron relaxation dynamics, and phonon contributions in TMC photophysics. These findings are crucial for NIR emitters' design, promoting TMCs' photo-reactivity to advance sustainable material development with abundant metals and flexible ligands³.

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(3) Forde, A.; Lystrom, L.; Sun, W.; Kilin, D.; Kilina, S. Improving Near-Infrared Emission of meso-Aryldipyrrin Indium(III) Complexes via Annulation Bridging: Excited-State Dynamics. *The Journal of Physical Chemistry Letters* 2022, 13 (39), 9210-9220. DOI: 10.1021/acs.jpcl.2c02115.