In Search of Mechanism of Aggregation-Induced Emission: A Theoretical Study

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Abstract: This study explores the fundamental photophysical origins of aggregation-induced emission (AIE) phenomenon[1] by examining the interplay of conical intersections (CIs) and restricted intramolecular motions (RIM) across diverse molecular systems. Using Spin-Flip TDDFT[2] with tuned and untuned range-separated hybrid (RSH) functionals,[3] the work reveals how molecular distortions enable non-radiative decay in solution, while aggregation suppresses these pathways to enhance emission. In styrene derivatives,[4] aryl-main axis rotation and C=C pyramidalization lead to twisted intramolecular charge transfer (TICT) states and CI-mediated quenching; in larger fused systems like tetrabenzoheptafulvalene derivative,[5] phenyl flapping accesses low-lying minimum energy conical intersections (MECIs); and in ethylene derivatives,[6] C=C twisting drives efficient internal conversion in the solution state. Upon aggregation, steric and electrostatic constraints restrict these motions, raising CI energies and resulting in intense luminescence. These findings establish the restriction of access to conical intersections (RACI)[7] as a unified mechanism of AIE, offering a mechanistic insight for designing new luminogens with tailored emission properties for optoelectronic, sensing, and bioimaging applications.

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