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Research Scholarship

Dynamics and Photophysics of Unconventional ESIPT Systems

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Abstract

This study explores the unconventional excited-state intramolecular proton transfer (ESIPT) reactions and their ultrafast dynamics across three distinct series of compounds: thiol-substituted flavones, enol-keto isomerization OLED emitters, and natural Nerviones.

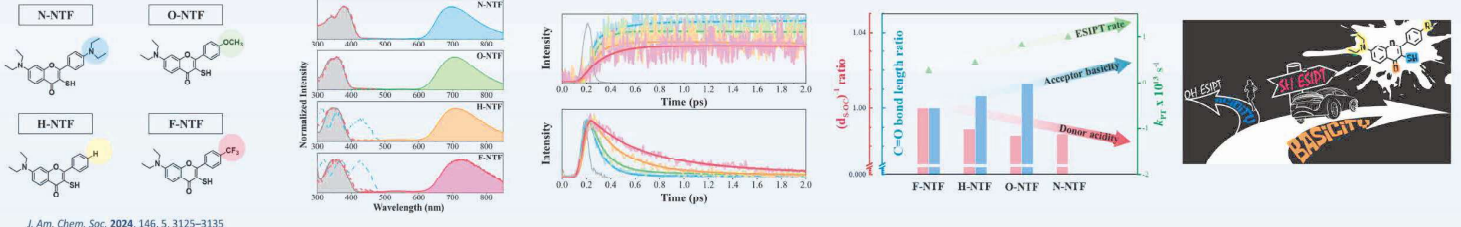
Part 1 investigates the thiol-related hydrogen bond (H-bond) and its ESIPT reaction in compounds such as 4'-diethylamino-3-mercaptopyrone (3NTP). These compounds exhibit ESIPT in both cyclohexane solution and solid state, producing a 710 nm tautomer emission with a remarkably large Stokes shift of 12,230 cm⁻¹. The study challenges traditional ESIPT models by demonstrating that the proton-accepting strength of thiol H-bond, rather than the S-H acidity, governs the ESIPT process. A new series of 4'-substituted-7-diethylamino-3-mercaptopyrone (NNTFs) was synthesized, revealing that the strongest H-bonded F-NTF displayed the slowest ESIPT rate, emphasizing the unconventional nature of thiol H-bonding systems.

Part 2 presents a novel series of ESIPT emitters, DPNA, DPNA-F, and DPNA-Bu, which are characterized by dual intramolecular hydrogen bonds. These compounds exhibit fast ground-state equilibrium among enol-enol (EE), enol-keto (EK), and keto-keto (KK) isomers, and ultrafast ESIPT leading to narrowband red OLED emission centered at about 670 nm with high photoluminescence quantum yields. Using transient grating photoluminescence (TGPL), the dynamics of ESIPT were resolved, demonstrating a highly efficient process suitable for fabricating deep-red OLEDs that meet the BT.2020 standard.

Part 3 details the first asymmetric total synthesis of Nervione (NV) and its demethylated derivative NV-OH, which exhibit unique ESIPT properties. The study reassigns the natural product NV based on circular dichroism discrepancies and explores the ESIPT behavior of NV-OH, showing excitation-wavelength-dependent dual emissions at 340 nm and 500 nm. The research uncovers anti-Kasha behavior and reversible ESIPT dynamics, establishing an equilibrium between normal and tautomer species. This work combines total synthesis with the discovery of new photophysical phenomena, highlighting the intricate relationship between hydrogen bonding and ESIPT.

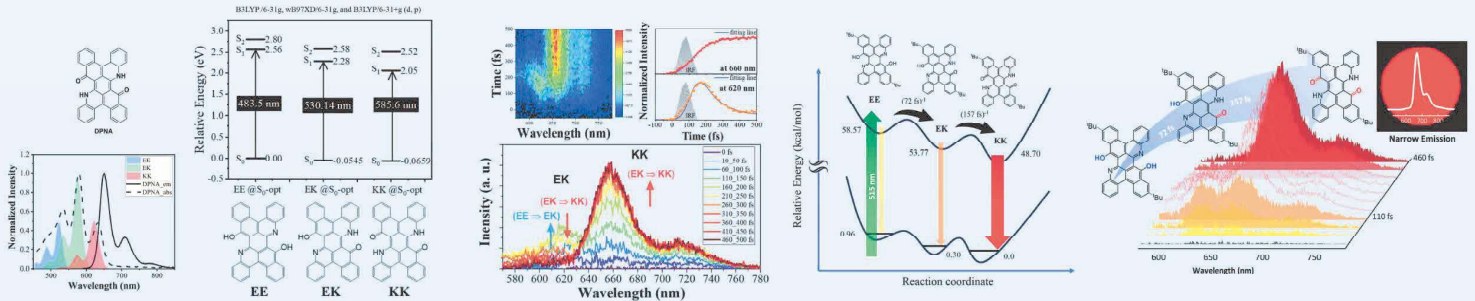
Collectively, this study provides deep insights into the mechanisms and applications of unconventional ESIPT systems, paving the way for advancements in photonic materials and technologies.

Part 1: Hydrogen-Bonded Thiol Undergoes Unconventional Excited-State Intramolecular Proton Transfer Reactions



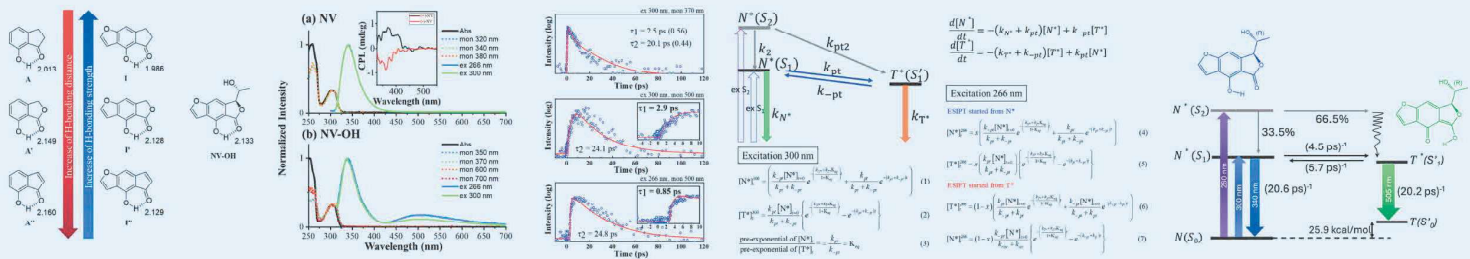
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Part 2: Multiple enol-keto isomerization and excited-state unidirectional intramolecular proton transfer generate intense, narrowband red OLEDs



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Part 3: Nerviones: total synthesis, structure reassignment and unique excited-state properties



Reflections on research life

Pursuing my Ph.D. has been both a rewarding and challenging journey, particularly as my master's research in lithium-ion batteries differed significantly from my current focus on spectroscopic dynamics. The transition was demanding, and the initial phase was marked by steep learning curves and numerous obstacles. However, my dedication to research and my enthusiasm for expanding my knowledge enabled me to persevere. Over time, these efforts culminated in meaningful progress and achievements. I am deeply grateful to those who have supported me throughout this journey. I extend my heartfelt thanks to my Ph.D. advisor, Professor Chou, for his willingness to accept me into his lab despite my limited experience in this field and for his invaluable guidance and mentorship. I am also thankful to my lab colleagues for their collaboration, encouragement, and shared commitment to our work. Furthermore, I appreciate the contributions of collaborating professors and students, whose support has been instrumental in advancing my research. I am equally grateful to my family and friends for their unwavering support and encouragement, and CTCI foundation for the research scholarship, which has provided significant motivation. Reflecting on this journey, I recognize the immense value of cross-disciplinary training and collaboration. Engaging with international scholars and participating in conferences have broadened my perspectives and enriched my academic experience. These opportunities have been intellectually stimulating and have fostered both personal and professional growth. While the path of research is often marked by challenges, I view these as opportunities for development. Each obstacle has contributed to my growth as a researcher and as an individual. Looking ahead, I aspire to continue refining my skills, contributing to my field, and embracing the challenges and opportunities that lie ahead.