

Title	トラップ誘起持続発光材料のメカニズムと応用
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# Abstract

In **Chapter 1**, I first explore the historical development of organic and inorganic Persistent Luminescence (PersL) materials, then review the major types of PersL materials and key breakthrough works, as well as their operating principles and typical applications.

**Chapter 2** provides a comprehensive overview of the fundamental theoretical principles underlying organic and inorganic long-lasting emission. The mechanisms of organic afterglow include: (1) afterglow resulting from triplet-to-singlet spin-forbidden transitions (phosphorescence and delayed fluorescence), (2) PersL arising from charge-separated states (electron transporting mode, hole transporting mode, and two-photon ionization), (3) trap-induced PersL, and (4) chemiluminescence. In the case of inorganic PersL, the mechanisms involve: (1) the electron trapping-detrapping model, (2) the hole trapping-detrapping model, and (3) the bandgap engineering effect. Furthermore, five stimulation methods are introduced for trap-induced PersL in both organic and inorganic materials, including: (1) thermal stimulation, (2) optical stimulation, (3) mechanical stimulation, (4) electrical stimulation, and (5) magnetic stimulation.

**Chapters 3-6** constitute the core of this thesis, structured as follows: Abstract, Introduction, Experimental Procedure, Results and Discussion, Conclusion, Reference, and Supporting Information. Notably, the problems or challenges in the PersL field, as well as the significance of the undertaken research works, will be thoroughly addressed in the 'Introduction' part. **Chapters 1-2** provide both the data support and theoretical foundation needed for the research topics. In trap-induced PersL systems, two key research targets emerge: trap and luminescent center. From a mechanistic perspective, **Chapter 3** primarily focuses on the depth regulation of trap states, while **Chapters 4-6** concentrate on the modulation of emission color and the excitation forms at the luminescent centers. From an application standpoint, **Chapters 3-4** emphasize optical information storage and anti-counterfeiting, whereas **Chapters 5-6** focus on the application of electroluminescent TTIs.

In **Chapter 3**, we introduced a novel TADF guest, incorporating electron-accepting naphthalimide with two cyan groups into a host-guest PersL system, revealing for the first time the link between molecular design and trap depth. The D-A-D wedge-shaped TADF emitter TCN was employed, enabling multi-mode excitation, deep traps, low aggregation-induced quenching, and high thermal stability. UV, visible light (425-630 nm), and X-rays efficiently triggered deep traps ( $\sim 0.72$  eV), closely matching theoretical calculations. TL at 385 K, with NIR stimulation up to 1300 nm, allowed retention for over 45 days. This multi-mode optical storage system extended applications to blue-laser writing, X-ray time-lapse imaging, and NIR electronic signatures.

In **Chapter 4**, inspired by charge separation in organic xCT systems and charge trapping/detrapping in inorganic PersL phosphors, we introduced xCT states and trap states into a host-guest organic system to achieve visible-light-charged NIR PersL. For the first time, xCT interactions enabled efficient charge separation across excitation wavelengths from 380 to nearly 700 nm. By engineering energy levels, we achieved NIR PersL with durations exceeding 4 hours in a pTAP@TPBi film, setting a record for organic systems. We also demonstrated a trap depth over 1.0 eV under visible light excitation. This approach, validated across various charge transfer aggregates, allowed tunable trap depths and emission wavelengths by adjusting electron-donating segments. Exploiting the exceptional light energy storage of organics, we proposed triple-mode NIR anti-counterfeiting using mobile phone flashlights and information storage *via* blue laser direct writing.

In **Chapter 5**, we used TIP in host-guest systems to create a unique OLED emission layer, achieving over 100 s of afterglow and 60 min of energy storage after charging with a direct current electric field. This marked a record for the longest electrically excited afterglow in light-emitting devices. The mechanism involved the capture of injected holes and electrons by luminescent centers and traps in the emission layer. The trap depth, measured at 0.24 eV under electrical charging, aligned with optical excitation results, confirming electrical charging as an efficient trigger for PersL. The

temperature-dependent decay and energy storage properties expanded OLED applications to TTIs.

In **Chapter 6**, we developed structurally optimized AC electroluminescent devices (ELDs) incorporating zinc sulfide PersL phosphors encapsulated in high-dielectric-constant alumina ( $\text{ZnS@AlOx}$ ), achieving AC-driven inorganic PersL for the first time. The PersL intensity in these devices lasted over 15 minutes post-AC charging, setting a record for electrically excited afterglow duration. The mechanism involved the capture of separated electrons by intrinsic defects in metal-doped ZnS under AC-driven hot-electron impact. The estimated trap depth of 0.32 eV under AC charging aligned with results from light irradiation, demonstrating the efficiency of electrical charging in triggering PersL. With temperature-dependent decay characteristics and over 24 hours of energy storage, these ELDs showed potential for applications as TTIs.

## Keywords

Persistent Luminescence, Trap State, Luminescent Center, Light Energy Storage, Thermal Stimulation