Concise Review of TADF: Basic Principles, Material Design, Prospective Applications, and the Role of ROMP in Polymer Synthesis

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Concise Review of TADF: Basic Principles, Material Design, Prospective Applications, and the Role of ROMP in Polymer Synthesis

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Abstract:
OLEDs have achieved significant efficiency advancements through the utilization of TADF materials, which leverage RISC to potentially reach up to 100% IQE. TADF materials convert non-emissive triplet excitons into light, addressing the limitations of traditional fluorescent and phosphorescent materials. Although small molecules have predominantly been the focus of TADF research, TADF polymers created via ROMP provide adjustable properties and compatibility with solution-based processing. This review discusses the basic principles of TADF, the design strategies for donor-acceptor systems, and the potential applications in various fields, including OLEDs, sensors, bioimaging, and therapeutics.

Keywords:
Thermally Activated Delayed Fluorescence; *Organic Light-Emitting Diodes*; *Ring Opening Metathesis Polymerization*; *Blue Emission, Sustainable Technology*

1. INTRODUCTION

OLEDs have revolutionized display technology with their high brightness, ease of production, and the pivotal role of the Emitting Layer (EML) in device performance. Despite their advantages, traditional luminescent materials such as fluorescent and phosphorescent compounds face limitations, prompting a quest for alternatives like TADF materials[1–4]. The TADF phenomenon, elucidated in the 1960s, garnered renewed attention upon its integration into OLEDs in 2009, offering the promise of achieving an IQE of up to 100%[5–8].

TADF materials exhibit a distinct luminescence mechanism where triplet excitons undergo RISC process, transitioning to a singlet excited state before emitting light. This unique mechanism enables efficient utilization of non-emissive triplet excitons, thus potentially overcoming the limitations of conventional fluorescent and phosphorescent materials. An illustrative summary of these pathways is presented in Fig 1.

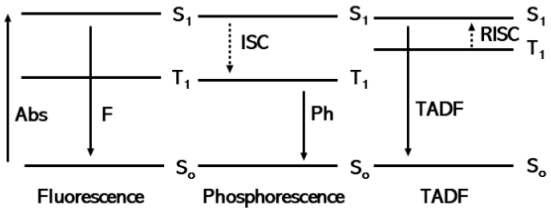

Fig 1. A schematic diagram comparing fluorescence, phosphorescence, and TADF is provided. Solid arrows illustrate emissive transitions, whereas dotted arrows denote up- or down-conversion processes, specifically intersystem crossing (ISC) and reverse intersystem crossing (RISC)[9].

While small molecules have historically dominated TADF research due to their facile synthesis and characterization, TADF polymers are increasingly being explored for their tunable properties and compatibility with solution-based processing techniques. ROMP method, known for its versatility in polymer synthesis, plays a crucial role in fabricating TADF polymers with tailored properties[10,11].

Living polymerizations are crucial for synthesizing polymers while preventing undesired termination, allowing precise control over molecular weight and microstructure. One widely used method is ROMP, which offers structural control, high tolerance to functional groups, and mild reaction conditions. ROMP polymerizes cyclic monomers, which can have various substituents, with ring strain often driving the polymerization process. Utilizing highly strained olefins minimizes the risk of secondary metathesis of the less-strained polymer backbone, leading to higher dispersity, unwanted side products, and decreased control over polymer architecture[12–18].

In this review, we aim to delve into the fundamentals and mechanisms of TADF, elucidate the design principles behind donor and acceptor systems in synthesized materials, and explore the potential applications of TADF materials in various optoelectronic devices. By understanding the intricacies of TADF materials and their applications, this approach can lay the groundwork for developing next-generation OLEDs and other advanced light-emitting technologies.

2. FUNDEMNTALS OF TADF

TADF represents a state-of-the-art photophysical mechanism that boosts OLED efficiency by utilizing both singlet and triplet excitons. The fundamental principle of TADF involves reverse intersystem crossing (RISC) from the triplet state (T_1) to the singlet state (S_1), driven by thermal energy. This process is feasible in molecules engineered to have a small energy gap (ΔE_{ST}) between the singlet and triplet states, enabling thermal energy at ambient temperature to overcome this barrier. Consequently, TADF materials can attain nearly 100% internal quantum efficiency by converting both singlet and triplet excitons into light. This remarkable efficiency positions TADF as a pivotal advancement for high-performance optoelectronic devices.

2.1 Mechanism of TADF

TADF involves a series of processes starting with electrical excitation, which creates excitons in high-energy states. These excitons quickly relax to the lowest energy states (S_1 or T_1) through internal conversion (IC). Singlet excitons can either emit light immediately via fluorescence or lose energy non-radiatively, or they can transition to triplet excitons through ISC. Triplet excitons cannot emit light directly as phosphorescence; instead, they return to the ground state non-radiatively or revert to singlet excitons via RISC, facilitated by thermal activation. This mechanism produces two types of fluorescence: prompt fluorescence (PF) originating from singlet excitons and delayed fluorescence (DF) from triplet excitons transitioning back to singlet states, both types exhibit distinct lifetimes yet share identical spectral profiles. A minimal singlet-triplet energy gap (ΔE_{ST}) is essential for effective RISC, facilitating nearly 100% internal quantum efficiency through the utilization of both singlet and triplet excitons. In OLEDs, TADF emitters generate 25% singlet and 75% triplet excitons through electron-hole recombination, and efficient conversion of triplet excitons to singlet excitons via RISC is essential for maximizing electroluminescence.

In OLED devices, excitons are generated in a 1:3 ratio of singlets to triplets following electron-hole recombination. Because triplets are more numerous and have longer lifetimes than singlets, an efficient RISC from T_1 to S_1 and a stable T_1 state are crucial for enhancing fluorescence efficiency Fig 2.

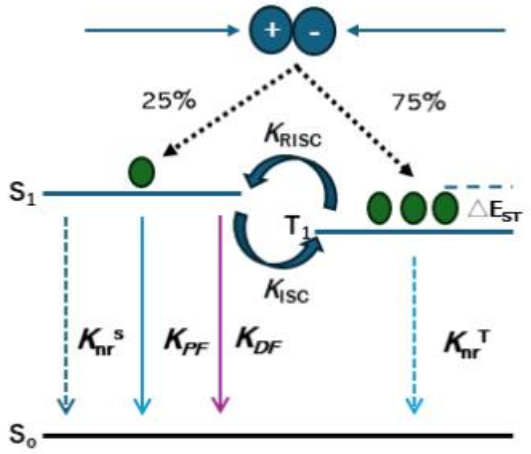

Fig 2. Diagram illustrating TADF processes via electroexcitation for OLEDs. (k_{nr}^S and k_{nr}^T: non-radiative decay constants of S_1 and T_1, respectively; k_{PF} and k_{DF}: rate constants of prompt fluorescence (PF) and delayed fluorescence (DF); k_{ISC} and k_{RISC}: rate constants of intersystem crossing (ISC) and reversible intersystem crossing (RISC). Phosphorescence is not considered.)

RISC is temperature-dependent, becoming more efficient at higher temperatures due to its endothermic nature, including a Boltzmann distribution relationship that describes the dependence of K_{RISC} on temperature:

$$k_{\mathrm{RISC}} \propto \exp\left(-\frac{\Delta E_a}{k_{\mathrm{B}}\, T}\right)$$

where k_B is the Boltzmann constant, T represents temperature, and ΔE_a denotes the activation energy, commonly referred to as the singlet-triplet splitting energy (ΔE_{ST}). Given that OLED devices operate at room temperature, T remains constant, underscoring the importance of a small ΔE_{ST} for efficient RISC.

2.2 Molecular Design.

In the design of TADF polymers, the selection of appropriate functional groups is pivotal. Various functional groups, such as electron donors and acceptors, are strategically integrated to achieve the TADF effect. Typically, electron donors in D-A type TADF polymers include N-containing aromatic groups known for their strong electron-donating capabilities, requiring high triplet energy levels, stability, and efficient carrier transport properties. Common electron donors include acridine, aniline, carbazole, phenoxazine, and their derivatives. Electron acceptors typically consist of nitrogen heterocycles, diphenylsulfones, cyanobenzenes, and their derivatives, valued for their potent electron-withdrawing properties, effective electron conjugation, and modifiable molecular structures **Fig 3**.

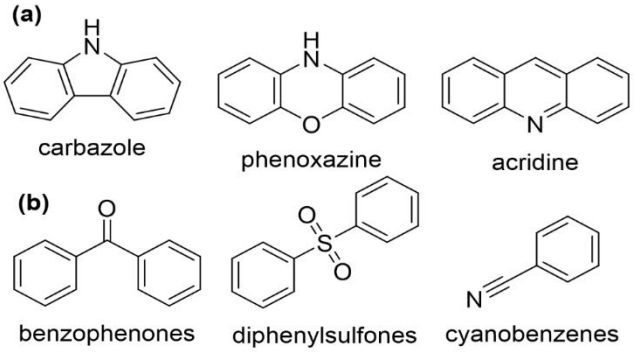

Fig 3. structures of various (a) donor units and (b) acceptor units.

TADF materials are developed using three primary strategies: through space charge transfer (TSCT), twisted intramolecular charge transfer (TICT), and multiple resonance (MR) TADF Fig 4.

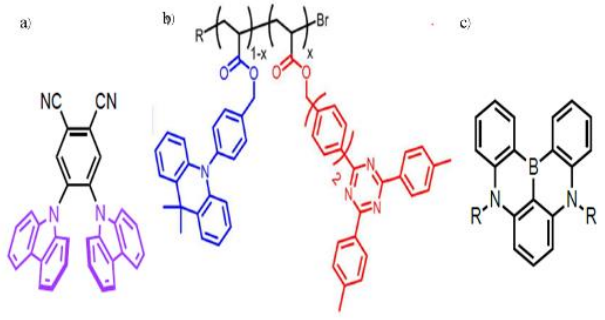

Fig 4. Representative structures of the three main types of TADF design: a) TICT, b) TSCT, c) MR-TADF[19].

Each of these methods seeks to reduce the singlet-triplet energy gap ΔE_{ST} by spatially segregating the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) through distinct methods. In both TICT and TSCT TADF materials, a donor-acceptor dyad structure is common, where the electron-rich donor hosts the HOMO, and the electron-poor acceptor hosts the LUMO. To minimize the overlap between HOMO and LUMO, these components are often made sterically bulky or are separated by linkers, typically resulting in a twisted configuration with a near-orthogonal orientation between the donor and acceptor. The most frequently reported TICT TADF emitters leverage this twist to minimize orbital overlap and facilitate efficient RISC[20].

A significant example of this design strategy was demonstrated by Adachi [21]. They utilized cyano-substituted aromatic acceptors paired with carbazole donors to produce highly efficient TADF emitters. The steric hindrance created between the donor and acceptor in these compounds induced a twist, effectively localizing the HOMO on the donor and the LUMO on the acceptor, thus achieving a small ΔE_{ST} and enhancing TADF efficiency. Cyano groups played a crucial role by preventing non-radiative decay and stabilizing the geometric configuration between the S_1 and triplet T_1 states, further contributing to the overall efficiency of the TADF process.

3. SYNTHESIS STRATEGIES FOR TADF VIA ROMP

The synthesis of TADF materials via ROMP involves designing monomers with TADF-active units, such as carbazole, acridine, or triazine derivatives, which are polymerized using transition metal catalysts like Grubbs' catalysts. This method allows precise control over polymer architecture through copolymerization and post-polymerization modification, optimizing the physical and electronic properties of the resulting materials. Recent advancements in ROMP techniques, including the development of functionalized catalysts, block copolymerization, and living ROMP, have enabled the creation of well-defined TADF polymers with enhanced performance, accelerating their application in optoelectronic devices and beyond **Fig 5.**

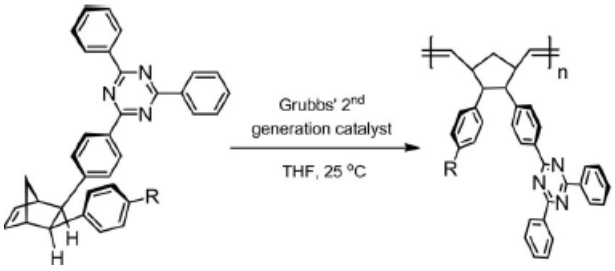

Fig 5. Synthesis of through-space charge transfer polynorbornenes[10].

4. UTILIZED TECHNIQUES

The characterization of TADF materials produced through ROMP encompasses a variety of techniques to assess their photophysical properties, thermal robustness, and device performance. Spectroscopic methods, such as UV-Vis, photoluminescence (PL), time-resolved photoluminescence (TRPL), and electroluminescence (EL) spectroscopy, are employed to investigate absorption spectra, emission behavior, and exciton dynamics. Thermal stability and phase transitions are assessed through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Additionally, device performance is gauged through current-voltage-luminance (I-V-L) measurements and device longevity testing, which provide critical insights into the electrical characteristics and durability of TADF materials in OLED applications. Together, these techniques offer comprehensive data essential for optimizing TADF materials for high-efficiency and stable optoelectronic devices.

5. APPLICATIONS OF TADF MATERIALS

TADF materials have found diverse applications across several fields due to their unique luminescent properties and operational advantages.

4.1 Oldes

TADF materials have revolutionized the field of OLEDs, offering significant advantages over traditional phosphorescent and fluorescent emitters[22]. In OLEDs, TADF emitters facilitate effective utilization of both singlet and triplet excitons, thereby enhancing device efficiency and reducing energy losses **Fig 6.**

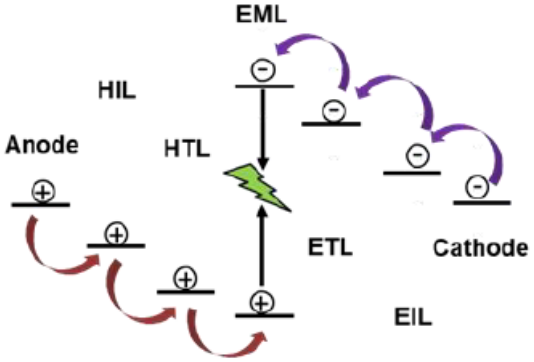

Fig 6. working principle of electroluminescence in shown OLED configuration.

The utilization of TADF materials has led to the development of OLEDs with improved brightness, color purity, and operational lifetimes. These materials are particularly advantageous in flexible and foldable display technologies, where their low power consumption and high efficiency are critical.

4.2 Sensors

TADF materials have gained attention as versatile components for sensor applications due to their unique delayed fluorescence and sensitivity to environmental changes. These sensors leverage TADF's delayed emission to detect various analytes by observing changes in fluorescence intensity or lifetime, making them ideal for chemical, biological, and environmental sensing. In chemical sensors, TADF materials are employed to detect specific gases and volatile organic compounds

(VOCs) in real-time, playing an essential role in environmental monitoring and industrial safety. In biological sensors, TADF materials enable accurate detection of biomolecules such as proteins and DNA/RNA sequences, which supports medical diagnostics and biotechnological research Fig 7.

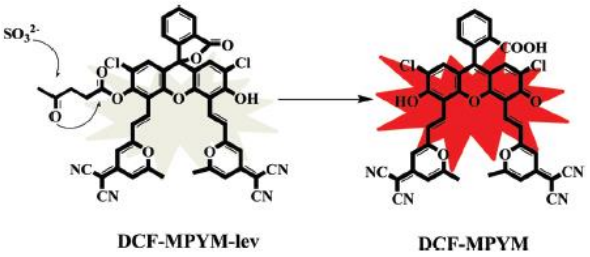

Fig 7. The response mechanism of the chemosensor DCF-MPYM-Lev

These sensors benefit from the high sensitivity, selectivity, rapid response times, and durability of TADF materials, making them promise advancements in sensor technology across multiple fields. Research continues to improve TADF materials' performance and broaden their applications in cutting-edge sensing devices[23].

5.3 Bioimaging

Due to their remarkable luminescent properties, TADF materials are increasingly prominent in bioimaging applications. They provide high photostability and low cytotoxicity, which make them suitable for prolonged imaging studies and live cell applications. The delayed fluorescence of TADF materials improves imaging sensitivity and contrast by minimizing background noise from biological tissues. This enables precise detection of low-abundance biomolecules and subtle biological changes, crucial for early disease detection and monitoring cellular processes Fig 8.

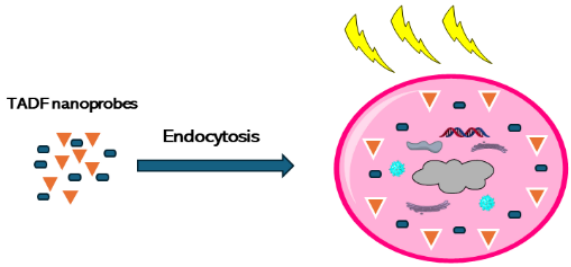

Fig 8. Representation of the preparation of TADF nanoprobes for imaging.

TADF materials are used in cellular imaging to study organelles and proteins, in tissue imaging to identify cancerous tissues and map vascular networks, and in in vivo imaging for real-time tracking of disease progression and therapeutic responses. Current research focuses on enhancing the brightness, stability, and specificity of TADF materials, with potential advancements including targeted functionalities and multimodal imaging capabilities[24].

5.4 Therapeutics

Due to their unique photophysical properties, TADF materials are increasingly utilized in therapeutic applications. They play a significant role in photodynamic therapy (PDT) for cancer treatment, leveraging stable luminescence to produce reactive oxygen species (ROS) that specifically target and eliminate cancer cells while minimizing harm to healthy tissues. Additionally, TADF materials facilitate controlled, light-activated drug release in drug delivery systems, enhancing precision and reducing side effects. Their use in imaging-guided therapy allows for real-time visualization and adjustment of treatments, ensuring accurate targeting of tumors or diseased tissues Fig 9.

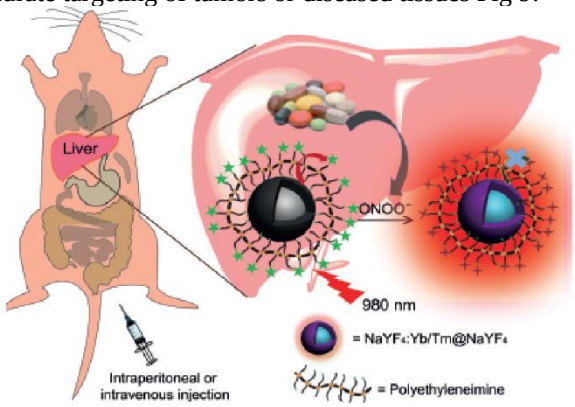

Fig 9. Designing chromophore-assembled UCNPs for detecting nitrosative hepatotoxicity in vivo.

The advantages of TADF materials, such as targeted activation, minimized side effects, high photostability, and versatile chemical modifiability, make them valuable tools in advancing precision medicine and improving therapeutic efficacy across various medical applications[25].

5. CONCLUSIONS

In conclusion, TADF materials offer a transformative pathway for OLEDs, utilizing non-emissive triplet excitons to enhance IQE. TADF polymers, synthesized via ROMP, promise scalable and versatile optoelectronic materials. Continued research into TADF mechanisms and material design will advance OLED performance and sustainability, shaping the future of optoelectronics. Furthermore, TADF materials hold promise for diverse applications including OLEDs, sensors, bioimaging, and therapeutics.

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