A BRIEF OVERVIEW OF THERMALLY ACTIVATED DELAYED FLUORESCENCE (TADF) LIGHT EMITTING ELECTROCHEMICAL CELLS (LEECs)

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Thermally Activated Delayed Fluorescence Light-Emitting Electrochemical Cells (TADF-LEECs) are single-layer emitters in which the active film contains both a luminophore and mobile ions (either an ionic TADF emitter or a neutral TADF host mixed with a salt/ionic complex). Under bias voltage, the ions migrate and form electrical double layers (EDLs) at the electrodes, lowering the injection barriers. Subsequent electrochemical doping (p-type near the anode, n-type near the cathode) creates a dynamic p-i-n junction with radiative recombination inside the film. The TADF mechanism- a small ΔE_{st} that enables thermally driven reverse intersystem crossing (rISC), allows the harvesting of singlet and triplet excitons without heavy metals, which in principle enables an internal quantum efficiency close to unity. Compared to multilayer OLEDs, TADF-LEECs offer a simpler architecture, fully solution-based fabrication compatible with print/roll, air-stable electrodes, and straightforward color tuning via the composition of the mixed layer. Remaining challenges include turn-on delay (ion migration), operational stability/lifetime and aggregation/dexter-type quenching at high doping levels. Effective design therefore targets high PLQY of the film, small ΔE_{ST}, controlled ionic conductivity, rigid matrix with appropriate T_g, and appropriate alignment of energy levels in host-guest systems.

Keywords: TADF, LEECs, Emitter, PLQY, EQE

Introduction. Light-emitting electrochemical cells (LEECs) are a class of electroluminescent devices that achieve efficient charge carrier injection and recombination using mobile ions within a single emitting layer [1]. When biased, the ions migrate to the electrodes and form electrical double layers (EDLs) that collapse the injection barriers. The continued ion movement leads to in situ electrochemical doping of the p-type near the anode and the n-type near the cathode, forming a dynamic p-i-n junction within the active film. This self-organized junction relaxes the thickness and work function constraints compared to multilayer OLEDs and enables simple device stacks, fully solution-based fabrication compatible with printing and roll-to-roll, and the use of air-stable electrodes [2]. Despite these advantages, LEECs have historically faced challenges related to turn-on delay (which is determined by ion mobility), operational stability, and quenching at high ion or dopant charges, which has led to material and architectural innovations that improve radiation efficiency and charge balancing without compromising simplicity [3]. Thermally activated delayed fluorescence (TADF) has proven to be a powerful way to increase internal quantum efficiency while avoiding heavy metal emitters. In TADF luminophores,

a small singlet-triplet gap (ΔE_{ST}) enables thermal up-conversion by reverse intersystem crossing (rISC), so that both singlet and triplet excitons can be harvested as fluorescence, in principle with up to 100% internal efficiency [4]. Molecular designs that spatially separate the highest occupied and lowest unoccupied molecular orbitals- typically donor-acceptor architectures- reduce ΔE_{ST} while maintaining sufficient oscillator strength and rigidity to sustain fast radiation rates and suppress non-radiative decay. In the solid state, aggregation-induced emission (AIE) and high glass transition temperatures (T_g) can further increase the photoluminescence quantum yield (PLQY) by restricting molecular motion and suppressing aggregation-induced quenching (ACQ) [5]. These TADF-cantered design principles naturally fit the requirements of LEECs: a single mixed layer must simultaneously support ion transport, balanced electrochemical doping, and bright emission under electrical strain. The combination of TADF emitters with the LEEC platform (TADF-LEECs) therefore represents a compelling route to efficient and fabrication-friendly devices. Two complementary material strategies were investigated. The first uses ionic TADF emitters, where the luminophore itself provides mobile counterions for EDL formation; this minimizes the inert salt content but can complicate molecular design and film morphology. The second approach uses neutral TADF hosts mixed with ionic species- salts or cationic metal complexes- so that the ions enable EDLs/doping while the organic emitter provides high PLQY fluorescence. In the latter approach, cationic iridium (III) complexes have played a dual role: (i) they provide mobile ions and facilitate electrochemical doping by improving injection and charge balance; and (ii) depending on energy orientation and concentration, they can participate in energy transfer or co-emission, providing additional opportunities for tuning colour and recombination zones. Careful host-guest engineering is therefore key aligning the frontier orbital energies to favour the formation of excitons on the TADF host, controlling the dexter/charge transfer pathways that cause quenching, and identifying an optimal dopant content that maximizes PLQY and device performance metrics (EQE, current efficiency, power efficiency) [6]. Another lever that has not yet been sufficiently explored is positional isomerism within donor-acceptor constructions. Donor-acceptor-donor′ (D-A-D′) architectures allow fine control over orbital overlap, molecular stiffness and packing through the choice of donor identity and linkage pattern (e.g., meta vs. ortho). Such structural changes can shift ΔE_{ST}, modify rISC kinetics, and influence aggregation behaviour, which in turn affects colour stability, exciton confinement, and device performance. The inclusion of mechanochromic responses in these emitters can additionally serve as a probe for packaging-dependent photophysics and provide insight into the effects of processing and post-processing on emission states in working films. Against this background, TADF-LEECs represent a promising convergence of mechanism and manufacturability: Ion-assisted charge injection and dynamic doping meet triplet harvesting without heavy metals. The

key scientific and technological questions now are how to (i) maximize PLQY in the solid state under ionic conditions, (ii) maintain small ΔE_{ST} with robust radiation rates, (iii) regulate ionic conductivity to minimize turn-on time and hysteresis while maintaining film integrity, and (iv) establish structure-property-performance relationships that predict colour behaviour and efficiency across different doping levels [7]. Answering these questions will advance LEECs from laboratory demonstrations to scalable, colour-stable, and energy-efficient lighting and display technologies.

Results and Discussion. The Fig. 1. summarizes the photophysical cycle of the TADF in relation to the LEECs. The blue lines labelled S_0, S_1 and T_1 denote the electronic energy levels: the ground state (S_0), the lowest singularly excited state (S_1) and the lowest triplet excited state (T_1). The vertical thick arrow of $S_1 \rightarrow S_0$ stands for fluorescence (radiative decay) [8]. The curved arrow from $T_1 \rightarrow S_1$ is the reverse intersystem crossing (rISC), the characteristic step in TADF. The small gap marked ΔE_{ST} indicates that singlet-triplet energy splitting is intentionally minimized by molecular design (typically donor-acceptor architectures) so that thermal energy at room temperature can carry triplets back to S_1 [9]. The "+ / –" symbols above indicate the mobile ions in a LEEC that allow ionic charge injection and in situ electrochemical doping under bias. When a voltage is applied in a LEEC, cations and anions migrate to the cathode and anode, respectively, forming electrical double layers (EDLs) [10]. These EDLs collapse the injection barriers so that electrons and holes are efficiently injected into the emitting layer. The continued ion movement leads to p- and n-type electrochemical doping near the anode and cathode, resulting in a dynamic p-i-n junction. In the intrinsic region, the injected charge carriers recombine to form excitons: a statistical mixture of singlets and triplets (generally approximated as 1:3). This step is implicit in the figure: The charge carriers form S_1 and T_1 populations that feed the TADF cycle. TADF cycle and why ΔE_{ST} is important. Immediately after excitation, part of the population occupies S_1 and decays radiatively, resulting in prompt fluorescence (nanoseconds) [11]. A comparable or larger part converts from S_1 to T_1 by intersystem crossing (ISC) (often not drawn, but complementary to rISC). When ΔE_{ST} is small (typically ≤ 0.1 eV), ambient thermal energy enables rISC ($T_1 \rightarrow S_1$), repopulating S_1 and resulting in delayed fluorescence (microsecondsto-milliseconds). Since triplets are "recycled" into singlets, both spin manifolds contribute to emission without heavy metals. In the ideal case - with small ΔE_{ST}, efficient rISC and suppressed non-radiative decay- the internal quantum efficiency (IQE) can be close to one [12]. Competing paths and effects on the device. If ΔE_{ST} is too large or the matrix is too flexible, rISC slows down and triplets may be lost at high exciton densities due to non-radiative channels (internal conversion, vibrational quenching) or Dexter annihilation. The ionic environment of a LEEC can be both helpful and complicating: EDLs and doping improve carrier balance, but local polarity and ion clustering can disrupt

energy levels and packing. The emphasis on a small ΔE_{ST} in the figure therefore highlights the key design trade-off: reducing the HOMO-LUMO overlap to reduce ΔE_{ST} (and thus support rISC), but maintaining sufficient oscillator strength and stiffness to keep radiation rates high and non-radiative motion low [13]. The arrow $S_1 \rightarrow S_0$ suggests high PLQY in fixed films when motion is constrained (e.g., AIE-like behaviour or a rigid host). The curved arrow $T_1 \rightarrow S_1$ predicts a delayed component in the time-resolved emission and a characteristic temperature dependence (delayed intensity and lifetime typically increase with temperature up to a certain point). For EL, successful rISC is evidenced by a higher EQE at a given brightness, a lower efficiency drops (when triplet management is effective) and, for mixed host-guest systems, spectral signatures of energy transfer or co-emission when a dopant is present. Design notes encoded in the sketch. To realize the scheme, the materials should have (i) small ΔE_{ST} (donor-acceptor separation, meta-linking or multiple resonance strategies), (ii) high rigidity/high T_g to suppress non-radiative decay, (iii) provide good energy alignment with electrodes/dopants to confine excitons to the intended emitter, and (iv) have moderate ionic conductivity to allow EDLs/dopants to form rapidly without causing morphological instability.

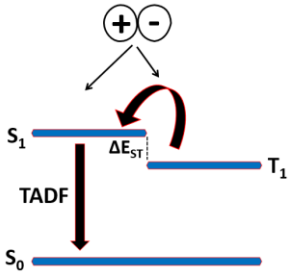

Fig. 1. TADF mechanism as a type of emitter

Aggregation-induced emission describes luminophores that are weakly or non-emissive as isolated molecules in good solvent, yet become strongly luminescent upon aggregation in poor solvent, in viscous media, in the solid state, or in polymer/host matrices. This behaviour is the inverse of the common aggregation-caused quenching (ACQ) seen in many planar π-systems [5]. AIE is valuable because virtually all optoelectronic devices emit from condensed phases (films, crystals, blends). Luminophores that brighten when immobilized naturally deliver higher solid-state PLQY, better colour stability, and reduced self-quenching [14]. The leading explanation is Restriction of Intramolecular Motion (RIM): in solution, low-frequency rotations/twists (phenyl "rotors," donor/acceptor dihedrals, vibrational modes) open fast non-radiative decay channels from S_1, giving weak emission [15]. Upon aggregation—or when embedded in a rigid matrix, these motions are hindered, suppressing internal

conversion and funnelling population into the radiative $S_1 \rightarrow S_0$ pathway. Variants include RIR (rotation), RIV (vibration), and RIT (torsion). Depending on structure, suppression of TICT (twisted intramolecular charge transfer) states can also boost emission by preventing a dark, strongly solvent-stabilized minimum. AIE does not require crystallinity, but crystallization-induced emission (CIE) is a common special case were packing locks motions most effectively [16]. PL intensity first drops slightly (dilution) then rises sharply when water fraction triggers nano aggregation; parallel DLS confirms particle formation. In thin films, AIE appears as PLQY (film) $\gg$ PLQY (solution) and often longer fluorescence lifetimes (reduced non-radiative rate). Temperature and viscosity dependences (cooling or adding glycerol) that increase PL further support RIM. Single-crystal/X-ray or MD simulations can reveal packing-enforced dihedral restrictions, intramolecular H-bonding, or steric locks consistent with AIE.

1. Propeller/rotor–stator motifs (e.g., tetraphenylethylene, hexaphenylsilole; donor–acceptor frameworks with rotatable aryls) encourage motion in solution and restriction in aggregates.
2. Built-in steric hindrance (tert-butyls, ortho substituents) frustrates π–π stacking that causes ACQ, while promoting loose, void-rich packing that immobilizes key dihedrals.
3. Rigidification handles (intramolecular H-bonds, spiro links, macrocyclic clamps) suppress non-radiative modes without sacrificing oscillator strength.
4. Balanced ICT: maintain enough donor–acceptor separation to tune colour and ΔE_{ST} (if TADF is desired) but avoid an excessively stabilized, dark TICT state.
5. Host/matrix engineering: high-T_g hosts or polymer backbones that mechanically "freeze" the emitter magnify the AIE gain in films.

For TADF emitters, AIE is especially synergistic. TADF needs a small ΔE_{ST} (reduced HOMO–LUMO overlap) yet still demands high radiative rates; AIE helps by rigidifying the excited state in the solid, suppressing non-radiative decay that would otherwise rise when charge-transfer character increases. In LEECs, where ionic species and electrochemical doping can plasticize films or perturb packing, an AIE-active emitter (or AIE-leaning host) helps retain high film PLQY under operational stress. Practically, you'll observe higher PLQY at an optimal dopant fraction; beyond that, excessive ionic/guest content may trigger ACQ or Dexter-type quenching, so AIE doesn't remove the need to optimize composition.

Conclusions. TADF-LEECs combine ion-assisted charge management with triplet harvesting, enabling efficient, color-tunable devices in a remarkably simple, fully solvable architecture. In this platform, mobile ions generate EDLs and a dynamic p-i-n junction under bias, while a TADF emitter with a small ΔE_{ST} recycles triplets via rISC, driving the internal quantum efficiency towards unity without heavy metals. The resulting materials and design picture is consistent and actionable: maximizing the PLQY of the film by stiffening the emitter and

utilizing AIE, maintaining a small ΔE_{ST} while preserving oscillator strength, regulating ion conductivity to allow EDLs/dopants to form rapidly without destabilizing morphology, and aligning energy levels to confine excitons to the intended luminophore. In mixed host-guest layers, ionic dopants (including cationic metal complexes) can simultaneously support injection/equilibrium and enable energy transfer or co-emission pathways, provided the dopant content is optimized to avoid ACQ/dexter quenching. Finally, positional isomerism (e.g., meta- vs. ortho-bonding in D-A-D′ frameworks) provides a powerful lever to optimize orbital overlap, rISC kinetics, aggregation behavior, and ultimately device color stability and efficiency. Looking ahead, the key challenges- turn-on delay, operational stability and quenching at high loads - should be addressed by (i) faster/bulkier ion designs or ion management interlayers to shorten ion transients, (ii) higher T_g or cross-linked matrices to suppress drift/plasticization, (iii) emitter frameworks that decouple small ΔE_{ST} from non-radiative motion (e.g., rigid D-A-D′ST), (iv) emitter frameworks that decouple small ΔE_{ST} from non-radiative motion and (v) emitter frameworks that decouple small ΔE_{ST} from non-radiative motion (e.g., rigid D-A-D′ST). E.g., rigid D-A-D′ or MR-TADF constructs) and (iv) spectrochemical operando tools that correlate EDL formation, doping profiles and EL spectra in real time. With these guidelines, TADF-LEECs are well positioned to evolve from laboratory demonstrations to scalable, color-stable, and energy-efficient illumination and display technologies compatible with printing and roll-to-roll manufacturing.

Acknowledgment. *This project has received funding from the Research Council of Lithuania (LMTLT), agreement No S-PD-24-82.*

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