International Tribology Council
Vytautas Magnus University
Lithuanian Scientific Society Department "Tribologija"

The 12th International Conference BALTTRIB'2024
21–23 November 2024
Akademija, Kaunas, Lithuania

Proceedings of BALTTRIB'2024 edited by prof. J. Padgurskas
eISSN 2424-5089 (Online)

DOI: 10.15544/balttrib.2024.12

INVESTIGATION OF MECHANOCHROMIC AND TRIBOLOGICAL PROPERTIES OF A NOVEL THERMALLY ACTIVATED DELAYED FLUORESCENCE CARBAZOLE DERIVATIVE FOR LIGHT-EMITTING ELECTROCHEMICAL CELL APPLICATION

M. Rabiei[1], J. Padgurskas, R. Rukuiza
Department of Mechanical, Energy and Biotechnology Engineering, Faculty of Engineering, Vytautas Magnus University, Studentu str. 15, Akademija, LT-53361 Kauno r., Lithuania

Abstract: This study investigates the design and synthesis of fish-shaped structures based on carbazole derivative for applications in light-emitting electrochemical cells (LEECs). A thermally activated delayed fluorescence (TADF) carbazole derivative was synthesized as an emitter in the active layer using a coupling reaction technique. $[Ir(buoppy)_2(dmapzpy)]PF_6$ was employed as a promising host, resulting in high-performance LEECs with enhanced brightness of 4952 $cd.m^{-2}$ and an external quantum efficiency (EQE) of 4.09%. The synthesized dye exhibited a lower singlet-triplet energy splitting (ΔE_{ST}) value of 0.06 eV compared to other reported counterparts, with reverse intersystem crossing (RISC) dominating its photophysical behavior. The crystalline dye demonstrated mechanochromic behavior, as its photoluminescence (PL) spectrum red-shifted upon mechanical stimulation. This mechanochromic behavior was also observed in the fabricated LEECs, and the tribological properties were further investigated.

Keywords: Carbazole; TADF; LEECs; RISC; Stimulation.

1. INTRODUCTION

Thermally activated delayed fluorescent (TADF) materials have emerged as promising candidates for next-generation organic light-emitting diodes (OLEDs), as they can achieve near-unity internal quantum efficiency without expensive heavy metal doping [1]. Among the various TADF frameworks, carbazole derivative have attracted much attention due to their excellent electronic properties, high triplet energy levels and strong hole transport ability [2]. Carbazole, with its rigid planar structure and electron-rich nature, serves as an effective donor moiety in donor–acceptor (D–A) systems, enabling efficient reverse intersystem crossing (RISC) from the triplet excited state (T_1) to the singlet excited state (S_1), thereby improving electroluminescence performance [3],[4]. The versatility of carbazole-based TADF emitters is due to their tunable photophysical properties, which can be adjusted by functionalizing the carbazole core with different acceptor moieties, such as benzophenone, triazine or cyano groups. These molecular modifications enable precise control of the singlet–triplet energy gap (ΔE_{ST}) and optimize the efficiency of exciton utilization in OLEDs [5],[6]. In addition, carbazole derivative have demonstrated remarkable stability, making them ideal for solution-fabricated and vacuum-deposited device architectures. Recent advances in the design and synthesis of carbazole-based TADF materials have led to the development of highly efficient blue, green and red emitters that overcome one of the biggest challenges in OLED research: achieving stable and efficient blue emission. In addition, the integration of carbazole units into hybridized local and charge transfer (HLCT) emitters has further improved the efficiency of the devices by balancing the radiative decay processes [7]. In this study, the basic design principles, synthesis strategies and optoelectronic properties of TADF-carbazole derivative are examined, highlighting their role in improving OLED performance. In addition, recent developments in host–guest systems, device engineering and stability considerations are discussed to provide insight into the future prospects of carbazole-based TADF materials for advanced display and lighting applications.

---

[1] Author for contacts:PhD. M. Rabiei
E–mail: rabieimarzieh7@gmail.com

2. CHEMICAL STRUCTURE OF DYE AND SYNTHESIS

The synthesis route of 10-(10-(4-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)-9,10-dihydroanthracen-9-yl)-10H-phenoxazine (Figure 1) is reported in Ref [8]. Taking into account the chemical structure of dye, a triphenylamine-based core with extended π-conjugation enhances electronic delocalization. The presence of a methoxy group (-OMe) acts as an electron donor and influences the HOMO-LUMO gap. The structure indicates a possible use in optoelectronics, e.g. in LECs. The electron-rich nature and the donor groups indicate possible charge transport properties. This molecule is likely intended for applications in organic electronics, including hole-transporting materials.

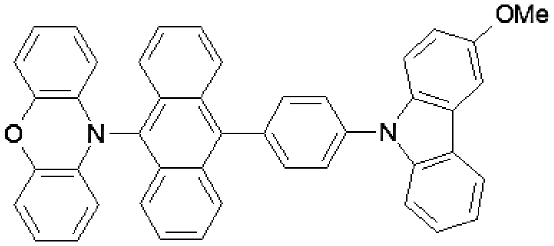

Figure 1. Molecular structure of dye [8].

3. ELECTROLUMINECENCE AND EFFECT OF SIMULATION

The schematic device structure of LEEC is shown in Figure 2. From left to right in the picture: ITO (indium tin oxide) as a transparent conductive anode. Transmits the emitted light while injecting holes into the device. Often used as the bottom electrode in optoelectronic devices. TFB (poly(9,9-dioctylfluorene-co-N-(4-butylphenyl)diphenylamine)) as a hole transport layer (HTL). It facilitates the transport of holes from ITO to the emitting layer and improves the performance of the device by equalizing the charge injection. The active layer is $[Ir(buoppy)_2(dmapzpy)]PF_6$ + dye, which is the central light-emitting layer. It contains a cationic iridium(III) complex, which serves as the emitter. The dye is mixed with the iridium complex to change the emission color or to improve the photophysical properties (e.g. PLQY). PF_6^- is the counter anion, that is important for ion mobility and the formation of the electrical double layer during operation. Al (aluminum) as the cathode material that feeds electrons into the emitting layer. Is usually deposited by thermal evaporation. The injection of charges into the emitting layer is driven by an external bias voltage. When a voltage is applied, electrons are injected from the Al cathode and holes from the ITO anode [9]. The device forms a p-i-n junction due to ion redistribution, which leads to recombination and light emission. Furthermore, the ions in the emitting layer (PF_6^- and the cationic iridium complex) migrate to the respective electrodes. This ion movement forms electrical double layers at both electrodes, reducing the injection barriers. Electrons are injected from the aluminum cathode and holes from the ITO/TFB side. The charges recombine in the emitting layer, resulting in electroluminescence [8]. After deposition of the emitter layer consisting of $[Ir(buoppy)_2(dmapzpy)]PF_6$ blended with a dye, the layer was exposed to toluene vapor for 2 minutes. This solvent vapor annealing process was employed to stimulate rearrangement, enhance film uniformity, and promote better molecular organization within the emissive layer. Such treatment can improve charge transport, phase separation, and overall electroluminescent performance of the device [10]. This stimulation can improve the efficiency of the device because: 1. Improved molecular packing and crystallinity The vapor from solvents allows the molecules in the emitter layer to reorganize or self-assemble into more ordered structures. Better molecular packing can improve charge transport, reduce trap states and promote the efficient formation and recombination of excitons. 2. Improved phase separation a mixture of emitter and host/dye, controlled stimulation promotes optimal phase separation at the nanoscale. This results in balanced charge injection and transport and minimizes losses due to charge recombination [9]. 3. Smoother film morphology the surface roughness can be reduced by vapor annealing, resulting in a more uniform and defect-free film. This improves the contact quality with the adjacent layers (such as HTL and cathode) and increases the efficiency of charge injection. 4. Reduction of residual solvents Controlled stimulation contributes to the evaporation of residual solvents trapped in the film, which could otherwise act as non-radiative recombination centers and reduce device lifetime and efficiency. 5. Improved energy transfer in cases where energy transfer between host and guest (or dye) is required, post-treatment improves the molecular interaction and promotes more efficient Förster or Dexter energy transfer. 6. Formation of a p-i-n junction (specific for LEECs) For LEECs, ion redistribution is key for the formation of the p-i-n junction in situ. An optimized and homogeneous film contributes to faster and more stable formation of the junction and improves turn-on time and brightness [11]. This stimulation (e.g. by solvent vapor or thermal treatment) can also improve the tribological properties of a film. This process changes the structure and surface of the film, resulting in better mechanical performance. The main effects include: Improved molecular packing – makes the film denser and more wear resistant. Smoother surface – reduces friction between contacting surfaces. Stronger adhesion to the substrate – prevents peeling or delamination under stress. Improved mechanical stability – increases durability and resistance to deformation [12], [13].

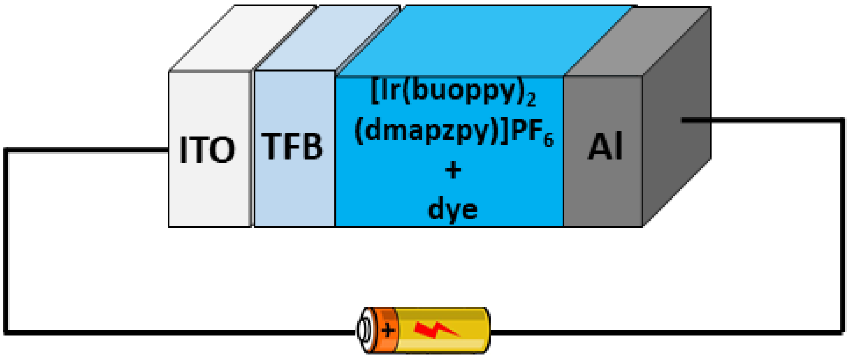

Figure 2. The devices structure.

In Figure 3-a, the EL spectra show almost identical peak positions (477 and 492 nm at 9 V) for both cases. Stimulation does not significantly change the emission color but slightly increases the intensity, suggesting better efficiency of charge recombination due to the improved film. In addition, the stimulated device (red line) in Figure 3-b shows higher current density than the unstimulated one at the same voltage, and stimulation improves charge transport and injection, probably due to smoother film morphology and better molecular organization, resulting in lower resistance and increased carrier mobility. The stimulated device achieves higher brightness at lower voltages. The improved film uniformity and charge equalization lead to more efficient exciton formation and radiative recombination, resulting in higher luminance at a given driving voltage (see Figure 3-c), when the turn-on voltage values of 8.24 and 8.46 V were achieved in tandem and the maximum brightness values of 4952 and 4634 cd.m^{-2} were reported for non-stimulated and stimulated devices, respectively. The summary of extracted values from EL properties are listed in Table 1. In addition, the stimulated device exhibits higher current efficiency over the entire brightness range, and the improved film quality decreases non-radiative losses and improves electron-hole recombination, resulting in better efficiency of electrical-to-optical light conversion in Figure 3-d. The EQE was improved when the devices were stimulated, and the maximum EQE was achieved at 4.71%.

Table 1. The extracted results from electroluminescence properties.

Device	**Turn on V, (V)**	**Maximum brightness, (cd.m^{-2})**	**Maximum CE, (cd.A^{-1})**	**Maximum PE, (lm.W^{-1})**	**Maximum EQE, (%)**	**Maximum EL, nm @ 9 V**
No stimulation	8.24	4952	9.11	5.08	3.69	477
With stimulation	8.46	4634	11.64	6.56	4.71	492

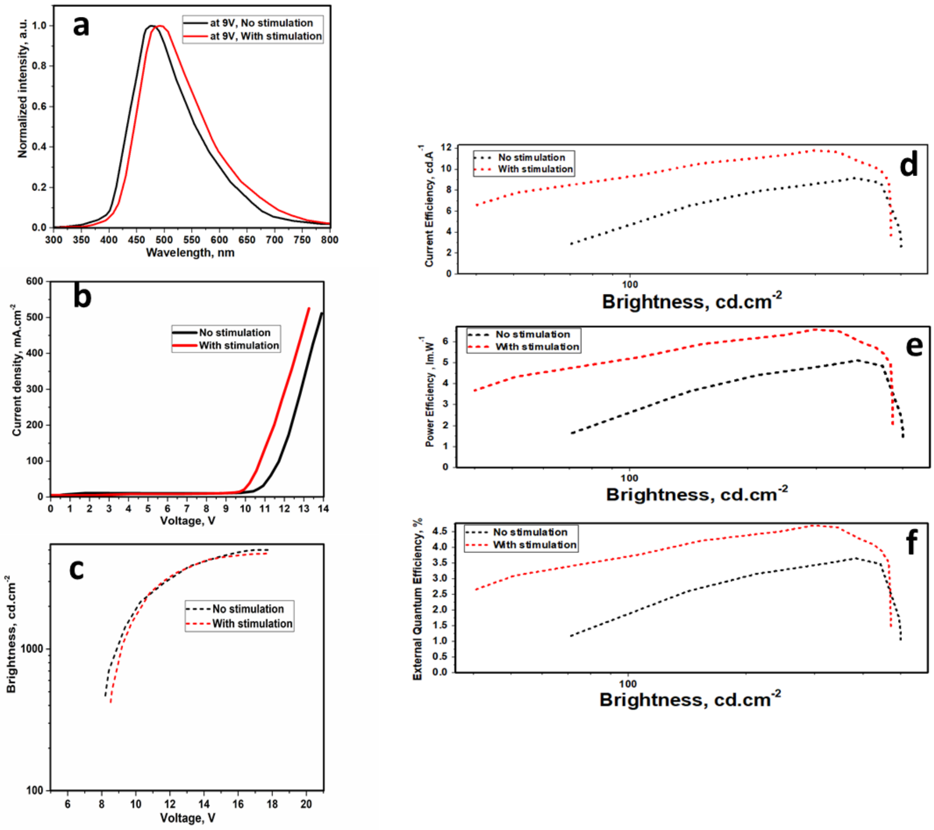

Figure 3. a) EL spectra, b) Voltage vs current density, c) voltage vs brightness, d), e), f) brightness vs CE, PR and EQE.

4. CONCLUSION

In this study, a novel carbazole derivative with thermally activated delayed fluorescence (TADF) was successfully synthesized and used as an active emitter material in LEECs. Integration of this dye with the host [Ir(buoppy)$_2$(dmapzpy)]PF$_6$ resulted in high electroluminescence performance. Solvent vapor stimulation with toluene significantly improved the film morphology, molecular organization and charge transport properties, resulting in improved current efficiency (11.64 cd.A^{-1}), power efficiency (6.56 lm.W^{-1}) and external quantum efficiency (4.71 %). The post-deposition stimulation treatment not only improved the optoelectronic properties of the device, but also contributed to better tribological behavior through smoother surfaces, stronger film adhesion and increased mechanical stability. Although the maximum brightness decreased slightly compared to the non-stimulated device, the overall performance metrics including EQE, CE and PE were significantly improved, confirming the effectiveness of the stimulation process. These results highlight the promising potential of combining TADF emitters with solvent vapor tempering strategies to develop efficient, stable and high performance LEECs for future optoelectronic applications.

ACKNOWLEDGMENT

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

REFERENCES

[1] Santos JM Dos, Hall D, Basumatary B, Bryden M, Chen D, Choudhary P, et al. The Golden Age of Thermally Activated Delayed Fluorescence Materials: Design and Exploitation. Chem Rev 2024;124:13736–4110. https://doi.org/10.1021/ACS.CHEMREV.3C00755.

[2] Zhu Y, Hao Y, Yuan S, Zhang F, Miao Y, Cui Y, et al. Improved light outcoupling of organic light-emitting diodes by randomly embossed nanostructure. Synth Met 2015;203:200–7.

https://doi.org/10.1016/J.SYNTHMET.2015.01.025.

[3] Yersin H. Highly Efficient OLEDs. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2018. https://doi.org/10.1002/9783527691722.

[4] Nobuyasu RS, Ren Z, Griffiths GC, Batsanov AS, Data P, Yan S, et al. Rational Design of TADF Polymers Using a Donor–Acceptor Monomer with Enhanced TADF Efficiency Induced by the Energy Alignment of Charge Transfer and Local Triplet Excited States. Adv Opt Mater 2016;4:597–607. https://doi.org/10.1002/ADOM.201500689.

[5] Ni F, Zhu Z, Tong X, Zeng W, An K, Wei D, et al. Hydrophilic, Red-Emitting, and Thermally Activated Delayed Fluorescence Emitter for Time-Resolved Luminescence Imaging by Mitochondrion-Induced Aggregation in Living Cells. Adv Sci 2019;6:1801729. https://doi.org/10.1002/ADVS.201801729.

[6] Wu S, Aonuma M, Zhang Q, Huang S, Nakagawa T, Kuwabara K, et al. High-efficiency deep-blue organic light-emitting diodes based on a thermally activated delayed fluorescence emitter. J Mater Chem C 2013;2:421–4. https://doi.org/10.1039/C3TC31936A.

[7] Rabiei M, Palevicius A, Ebrahimi-Kahrizsangi R, Nasiri S, Vilkauskas A, Janusas G. New Approach for Preparing In Vitro Bioactive Scaffold Consisted of Ag-Doped Hydroxyapatite + Polyvinyltrimethoxysilane. Polymers (Basel) 2021;13:1695. https://doi.org/10.3390/polym13111695.

[8] Rabiei M, Ghahary R, Hosseinnezhad M, Palevicius A, Vilkauskas A, Janusas G, et al. Light-emitting electrochemical cells based on mechanochromic, thermally activated delayed fluorescence fish-shaped structures consisting of carbazole derivatives as emitters in the active layer. Org Electron 2025;141:107214. https://doi.org/10.1016/J.ORGEL.2025.107214.

[9] Pal AK, Cordes DB, Slawin AMZ, Momblona C, OrtÍ E, Samuel IDW, et al. Synthesis, Properties, and Light-Emitting Electrochemical Cell (LEEC) Device Fabrication of Cationic Ir(III) Complexes Bearing Electron-Withdrawing Groups on the Cyclometallating Ligands. Inorg Chem 2016;55:10361–76. https://doi.org/10.1021/ACS.INORGCHEM.6B01602/SUPPL_FILE/IC6B01602_SI_002.CIF.

[10] Nasiri S, Dashti A, Hosseinnezhad M, Rabiei M, Palevicius A, Doustmohammadi A, et al. Mechanochromic and thermally activated delayed fluorescence dyes obtained from D–A–D′ type, consisted of xanthen and carbazole derivatives as an emitter layer in organic light emitting diodes. Chem Eng J 2022;430:131877. https://doi.org/10.1016/J.CEJ.2021.131877.

[11] Park S, Moon D, Damodharan SC, Chandran M, Choe Y. Iridium-based light-emitting electrochemical cells containing ionic liquids in the luminous layer. Mater Res Bull 2012;47:2807–10. https://doi.org/10.1016/J.MATERRESBULL.2012.04.122.

[12] Bartkowska A, Bartkowski D, Onufrijevs P, Grase L, Padgurskas J, Rukanskis M, et al. Anisotropy of the Tribological Performance of Periodically Oxidated Laser-Induced Periodic Surface Structures. Coatings 2023, Vol 13, Page 1199 2023;13:1199. https://doi.org/10.3390/COATINGS13071199.

[13] Halling J. The tribology of surface films. Thin Solid Films 1983;108:103–15. https://doi.org/10.1016/0040-6090(83)90496-0.