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DESIGN AND INVESTIGATION OF TADF CRYSTAL SURFACES DERIVED FROM CARBAZOLE AND PHENOXAZINE UNITS

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Abstract: Strategic structural designs to develop optical devices using columnar liquid crystal (CLC) frameworks are highly sought after. In this study, we report a novel luminescent material with multiple donor-acceptor units, comprising carbazole and phenoxazine derivatives. The material’s aggregation-induced emission (AIE) and triboluminescent (TL) properties were evaluated within a single molecule. Powder X-ray structural analysis revealed the presence of both amorphous and crystalline phases. The optical properties were shown to be systematically tunable through regulation of the material’s aggregation state, particularly with metastable positioning when the carbazole derivative was substituted. This study demonstrates that unique multifunctional characteristics can be integrated into a single compound by finely controlling its aggregation states, presenting a new strategy for exploring multifunctional organic materials. Luminescence and external quantum efficiency values reached 21850 cdm^{-2} and 4.7%, respectively.

Keywords: Carbazole; TADF; Phenoxazine; AIE; CLC, LEEC.

1. INTRODUCTION

Thermally activated delayed fluorescence (TADF) is a photophysical mechanism that enables the efficient generation of singlet and triplet excitons for light emission in organic materials [1]. In TADF emitters, the energy gap between the singlet (S_1) and triplet (T_1) states is very small, allowing reverse intersystem crossing (RISC) from T_1 back to S_1 upon thermal activation [2]. This process increases electroluminescence efficiency by utilizing triplet excitons without the need for heavy metal atoms. TADF materials are extremely attractive for OLEDs and LEECs as they offer a way to achieve near-unity internal quantum efficiency with purely organic compounds. Molecular design strategies for TADF typically involve donor–acceptor architectures that spatially separate HOMO and LUMO to reduce the energy gap between (S_1) and (T_1) [3]. Carbazole is an aromatic heterocyclic compound with the molecular formula $C_{12}H_9N$. It consists of a tricyclic structure made up of two benzene rings fused on either side of a five-membered nitrogen-containing ring. This rigid and planar structure gives it excellent electronic and photophysical properties that make carbazole and its derivatives very attractive for various applications in organic electronics and optoelectronics [4],[5]. Phenoxazine is a tricyclic heterocyclic compound with the molecular formula $C_{12}H_9NO$. It consists of an oxygen and a nitrogen atom integrated into a fused aromatic ring system, forming a structure analogous to phenothiazine, with the sulfur replaced by oxygen [6],[7]. Aggregation-induced emission (AIE) is a photophysical phenomenon in which certain molecules emit light more intensely in an aggregated or solid state than in dilute solution. Unlike conventional fluorophores, which suffer from aggregation-induced quenching (ACQ), AIE-active compounds are non-emissive in solution but become highly luminescent when they aggregate. This behavior is usually attributed to the restriction of intramolecular motions (RIM), which suppresses non-radiative decay processes in the aggregated state. AIE materials are extremely attractive for optoelectronic solid-state devices such as OLEDs, LEECs and sensors as they maintain or even enhance their emission during film formation. Molecular structures that favor AIE often include rotatable aromatic groups or non-planar geometries that are locked into emitting conformations upon aggregation [2],[8]. Columnar liquid crystals are a unique class of discotic liquid crystals in which disk-

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shaped molecules self-assemble into one-dimensional columns, which in turn organize into two-dimensional lattices. These materials combine the fluidity of liquids with the long-range ordering of crystals, making them ideal for organic semiconductors, photonic devices and light-emitting applications. Light-emitting electrochemical cells (LEECs) are a class of electroluminescent devices that emit light when an external voltage is applied. In contrast to OLEDs, LEECs contain mobile ions in the emitting layer, which play a crucial role in charge injection and light emission. As a result, LEECs are uniquely easy to manufacture, can be processed in solutions and are ideal for cost-effective and flexible lighting and display technologies [9], [10].

2. CLC TYPE OF STRUCTURE AND DESIGNED DYE

According to **Figure 1-a**, the black central disk represents a discotic core molecule, typically an aromatic unit. The colored side disks represent side chains or substituents, which may be flexible chains or functional groups. These molecules self-assemble through π-π stacking interactions and form one-dimensional columns. Depending on the molecule packing and symmetry, multiple columns arrange themselves into ordered arrays such as hexagonal, rectangular or slanted columnar phases [11]. Taking into account, this type of molecules, the dye was designed and synthesized (**Figure 1-b**). In **Figure 1-b**, the core is a 1,2,4,5-tetrasubstituted benzene ring that forms a symmetric and rigid scaffold. In addition, two arms contain phenoxazine residues, which are known for their strong electron donor ability and good hole transport properties. This architecture combines planar, π-conjugated donor units with a symmetric geometry that allows for potential π-π stacking and columnar organization in the solid state. The molecule contains phenoxazine and carbazole units, both known for their strong electron-donating properties and high triplet energy levels. These donor moieties are ideal for forming a donor-π-donor structure which contributes to: reducing the singlet–triplet energy gap, facilitating reverse intersystem crossing (RISC) enabling TADF behavior → efficient utilization of triplet excitons without metal complexes when the powder X-ray structural analysis revealed the presence of both amorphous and crystalline phases for dye. The symmetric, star-shaped architecture favors a columnar liquid crystalline organization that improves charge transport through π-π stacking, molecular orientation in thin films, and mechanical and morphological stability in solid-state devices. The side groups (phenoxazine, carbazole) improve the solubility in organic solvents. This makes the material compatible with solution methods such as spin coating or printing and ideal for cost-effective fabrication.

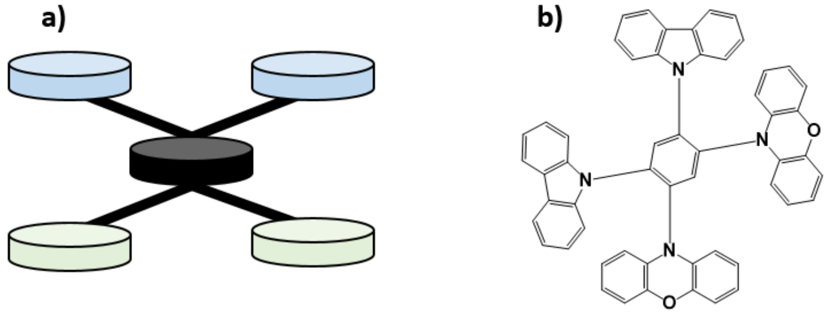

Figure 1. a) Schematic CLC structure and b) the chemical structure of designed CLC dye in this study.

3. OPTIMIZATION FROM DFT CALCULATION

Figure 2 shows a density functional theory (DFT) optimized geometry of a star-shaped organic molecule featuring a central benzene core substituted with four extended arms. The calculation was done by Gaussian 09W- DFT/6-311+G (d, p) [12]. These arms include heterocyclic donor moieties such as phenoxazine and carbazole-type fragments, connected through nitrogen linkers, as indicated by the presence of blue atoms (N). The molecule exhibits a twisted 3D geometry, which helps minimize π-π stacking in solution while enabling efficient packing and ordering in the solid state. The DFT optimization reveals a non-planar conformation, suggesting restricted intramolecular rotations, which can favor AIE or mechanochromic luminescence in condensed phases. The extended π-conjugated system and electron-rich donor units also make this molecule a potential TADF emitter, where a small singlet–triplet energy gap is desirable for reverse intersystem crossing (RISC). The HOMO and LUMO values were calculated as -5.63 and -2.71 eV respectively with singlet–triplet energy less than 0.05 eV. The calculated geometry serves as a foundation for further electronic structure analysis, including HOMO-LUMO energy levels, charge distribution, and excited-state properties, which are crucial for designing high-performance LEECs or OLEDs.

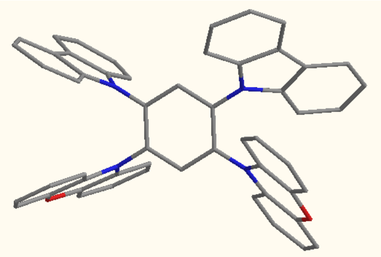

Figure 2. The optimized chemical structure of dye from DFT.

4. AIEE PHENOMENA

The phenomenon of aggregation- induced emission enhancement (AIEE) was observed when evaluating the PL intensity of mesible dyes in a THF-water mixture. The PL intensity increased when the water content was increased to 95 % (**Figure 3**). This graph shows the fluorescence emission spectra of the compound at different proportions of water (0 %, 50 %, 70 %, 80 %, 95 %). In pure solvent (0 % water) the emission is moderately strong. With increasing water content (up to 80 %), the emission intensity decreases, indicating quenching due to poor solubility and possible non-radiative decomposition. However, at a water content of 95% , the fluorescence intensity increases dramatically and shows a sharp peak at ~ 520 nm. This is a clear sign of AIEE. At high water content, the molecule aggregates and the restricted intramolecular motions suppress non-radiative pathways, resulting in enhanced fluorescence. In conventional fluorophores, aggregation often leads to fluorescence quenching due to strong π-π stacking or exciton annihilation this is called aggregation-induced quenching (ACQ). However, the opposite occurs with AIE-active molecules: Fluorescence is weak in solution but becomes strong upon aggregation. This phenomenon is primarily due to; 1) restriction of intramolecular motions (RIM) In solution, AIE molecules have rotatable groups or flexible structures. These internal motions do not dissipate the excitation energy by radiation, quenching the fluorescence. Upon aggregation, these motions are physically constrained by neighboring molecules. This blocks the non-radiative decay pathways and the energy is released as bright fluorescence. 2) Reduced π-π stacking AIE molecules are often designed with non-planar or twisted geometries. This prevents tight π-π stacking in the aggregated state. This avoids quenching (ACQ), which is common in planar aromatic systems, so that emission persists or increases. 3) Formation of radiatively excited states aggregation can favor the formation of J-aggregates (fluorescent) instead of H-aggregates (non-fluorescent). This molecular arrangement contributes to the stabilization of the radiatively excited states that contribute to light emission [13], [14], [15].

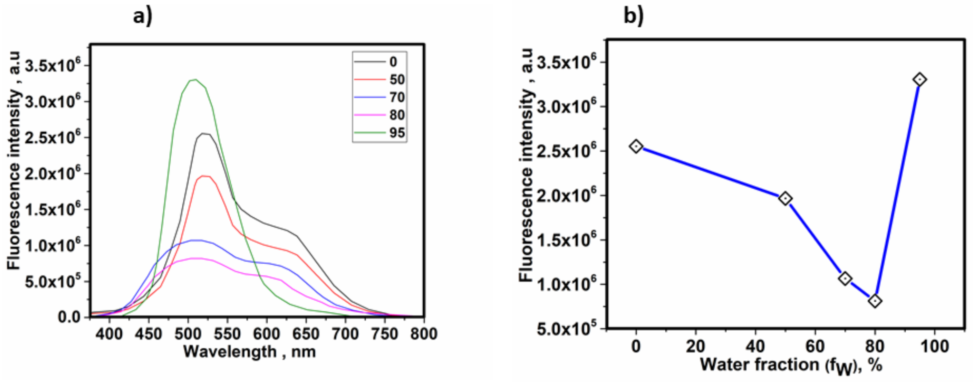

Figure 3. a) Proof of the AIEE mechanism, PL intensity of the dye-water:THF mixture at different water contents and b) water content vs. PL intensity of the miscible dye in water:THF

5. LEEC FABRICATION

Taking into account **Figure 4**, the device structures decorated is a LEEC consisting of a layered structure starting with an indium tin oxide (ITO) substrate. ITO acts as a transparent anode that both injects holes into the device and transmits the emitted light. A thin film of PEDOT:PSS is applied to the ITO layer to act as a hole injection and transport layer. This polymer blend helps to smooth the ITO surface and align its energy levels with the emission layer, improving hole mobility and ensuring a more balanced charge injection. The inclusion of a PEDOT:PSS layer improves surface smoothness and enhances adhesion between the ITO and the emissive layer, which may reduce the risk of delamination under mechanical stress. The heart of the device is the active layer, which consists of a cationic iridium(III) complex, [Ir(buoppy)$_2$(dmapzpy)]PF$_6$, mixed with a dye. This active layer is responsible for the light emission. The iridium complex is a highly efficient phosphorescent emitter that can harvest both singlet and triplet excitons. The presence of PF$_6$ as a counter ion plays a crucial role as it provides the ionic conductivity which allows the formation of electrical double layers at the electrode interfaces during operation. Moreover, the dye can be used to fine-tune the emission color or improve other photophysical properties such as the quantum yield of photoluminescence. At the top of the device, an aluminum electrode serves as a cathode that injects electrons into the emission layer under the influence of an externally applied voltage. As soon as a voltage is applied, the ions in the emitting layer migrate to their respective electrodes, that significantly lower the energy barriers for charge injection. This ion redistribution leads to the in-situ formation of a p-i-n junction, which enables efficient charge recombination in the emitting layer and leads to electroluminescence. This LEEC architecture combines solution-processable materials and ion-assisted charge injection to achieve stable and efficient light emission, making it a promising platform for low-cost and flexible optoelectronic devices. **Figure 5** shows the diagram of brightness and external quantum efficiency (EQE) as a result of the electroluminescence properties. The device shows a strong electroluminescence performance with a maximum EQE of 4.7 % at high brightness, followed by a slight decrease at very high luminance. This behavior indicates good material and device design, but also shows the importance of optimizing operating conditions to minimize efficiency losses at high brightness.

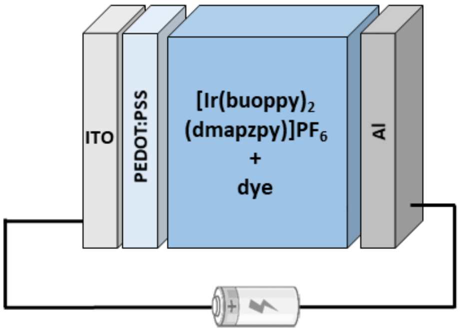

Figure 4. The device structure of LEEC.

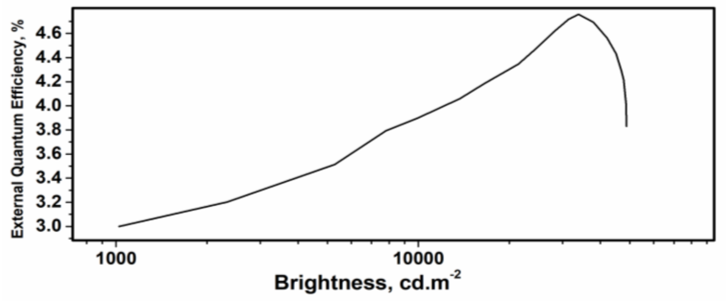

Figure 5. Brightness vs EQE as a result of EL properties.

6. CONCLUSION

In this study, a novel multifunctional organic emitter based on a columnar liquid crystal (CLC) with carbazole and phenoxazine donor units was successfully synthesized and characterized. The star-shaped architecture with a central benzene core enabled effective π-π stacking and columnar self-assembly favoring improved charge transport and structural stability in solid-state devices. The incorporation of phenoxazine and carbazole not only improved the solubility and hole transport properties, but also facilitated thermally activated delayed fluorescence (TADF) by reducing the singlet-triplet energy gap, as confirmed by DFT calculations. The compound exhibited pronounced aggregation-induced emission enhancement (AIEE) behavior due to restricted intramolecular motion and reduced π-π stacking in the aggregated state. The strong photoluminescence observed at high water contents emphasizes the AIE-active nature of the dye. The integration of this dye into the architecture of a light-emitting electrochemical cell (LEEC) using a cationic iridium complex as host resulted in efficient electroluminescence with a high external quantum efficiency (EQE) of 4.7 % and a maximum luminance of 21850 cdm^{-2}. The device showed strong performance under solution process fabrication conditions, confirming the potential of the material for low-cost, flexible and efficient optoelectronic applications. Overall, this work demonstrates a successful strategy for merging TADF, AIE and CLC properties in a single organic molecule, providing a promising route for the development of advanced materials for the next generation of solid-state lighting technologies.

REFERENCES

[1] P. Rajamalli, N. Senthilkumar, P. Gandeepan, P.Y. Huang, M.J. Huang, C.Z. Ren-Wu, C.Y. Yang, M.J. Chiu, L.K. Chu, H.W. Lin, C.H. Cheng, A New Molecular Design Based on Thermally Activated Delayed Fluorescence for Highly Efficient Organic Light Emitting Diodes, J. Am. Chem. Soc. 138 (2016) 628–634. https://doi.org/10.1021/JACS.5B10950/SUPPL_FILE/JA5B10950_SI_002.CIF.

[2] P. Palanisamy, M. Rabiei, M. Hosseinnezhad, A. Palevicius, G. Janusas, P.B. Managutti, S. Mohamed, L.E. de Sousa, L. de Thieulloy, P. de Silva, A. Vilkauskas, S. Nasiri, J.M. Nunzi, V. Nutalapati, Solution-Processed OLEDs Based on a Bipolar AIE Terpyridine Derivative as a Host, ACS Appl. Opt. Mater. 2 (2024) 76–87. https://doi.org/10.1021/ACSAOM.3C00346/SUPPL_FILE/OT3C00346_SI_002.CIF.

[3] J.M. Dos Santos, D. Hall, B. Basumatary, M. Bryden, D. Chen, P. Choudhary, T. Comerford, E. Crovini, A. Danos, J. De, S. Diesing, M. Fatahi, M. Griffin, A.K. Gupta, H. Hafeez, L. Hämmerling, E. Hanover, J. Haug, T. Heil, D. Karthik, S. Kumar, O. Lee, H. Li, F. Lucas, C.F.R. Mackenzie, A. Mariko, T. Matulaitis, F. Millward, Y. Olivier, Q. Qi, I.D.W. Samuel, N. Sharma, C. Si, L. Spierling, P. Sudhakar, D. Sun, E. Tankelevičiūtė, M.D. Tonet, J. Wang, T. Wang, S. Wu, Y. Xu, L. Zhang, E. Zysman-Colman, The Golden Age of Thermally Activated Delayed Fluorescence Materials: Design and Exploitation, Chem. Rev. 124 (2024) 13736–14110. https://doi.org/10.1021/ACS.CHEMREV.3C00755.

[4] T.D. Weinhold, N.A. Reece, K. Ribeiro, M. Lopez Ocasio, N. Watson, K. Hanson, A.R. Longstreet, Assessing Carbazole Derivatives as Single-Electron Photoreductants, J. Org. Chem. 87 (2022) 16928–16936. https://doi.org/10.1021/ACS.JOC.2C02312/SUPPL_FILE/JO2C02312_SI_001.PDF.

[5] V. Bhagyalakshmi, M. Indira, S.F. Banu, D. Venkateswarlu, V.K. Prasad, L.S. Sarma, C.S. Reddy, P.V. Govardhana Reddy, New conjugated carbazole derivatives: synthesis and photophysical properties catalysed by Pd–Cu@rGO, New J. Chem. 48 (2024) 3849–3861. https://doi.org/10.1039/D3NJ04408D.

[6] M. Almtiri, T.J. Dowell, I. Chu, D.O. Wipf, C.N. Scott, Phenoxazine-Containing Polyaniline Derivatives with Improved Electrochemical Stability and Processability, ACS Appl. Polym. Mater. 3 (2021) 2988–2997. https://doi.org/10.1021/ACSAPM.1C00152/SUPPL_FILE/AP1C00152_SI_001.PDF.

[7] K. Lee, I.E. Serdiuk, G. Kwon, D.J. Min, K. Kang, S.Y. Park, J.E. Kwon, Phenoxazine as a high-voltage p-type redox center for organic battery cathode materials: small structural reorganization for faster charging and narrow operating voltage, Energy Environ. Sci. 13 (2020) 4142–4156. https://doi.org/10.1039/D0EE01003K.

[8] N. Fei, Q. Wei, L. Cao, Y. Bai, H. Ji, R. Peng, L. Huang, H. Shiyou, Z. Ge, A symmetric nonpolar blue AIEgen as nondoped fluorescent OLED emitter with low efficiency roll-off, Org. Electron. 78 (2020) 105574. https://doi.org/10.1016/J.ORGEL.2019.105574.

[9] A.K. Pal, D.B. Cordes, A.M.Z. Slawin, C. Momblona, E. Ortí, I.D.W. Samuel, H.J. Bolink, E. Zysman-Colman, 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. 55 (2016) 10361–10376. https://doi.org/10.1021/ACS.INORGCHEM.6B01602/SUPPL_FILE/IC6B01602_SI_002.CIF.

[10] S. Hu, J. Gao, Materials and physics of light-emitting electrochemical cells (LECs), Handb. Org. Mater. Electron. Photonic Devices, Second Ed. (2019) 727–757. https://doi.org/10.1016/B978-0-08-102284-9.00022-X.

[11] T. Kato, T. Yasuda, Y. Kamikawa, M. Yoshio, Self-assembly of functional columnar liquid crystals, Chem. Commun. (2009) 729–739. https://doi.org/10.1039/B816624B.

[12] M.J. Frisch, J.A. Pople, J.S. Binkley, Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets, J. Chem. Phys. 80 (1984) 3265–3269. https://doi.org/10.1063/1.447079.

[13] N. Meher, P. Krishnan Iyer, N. Meher, P.K. Iyer, Spontaneously Self-Assembled Naphthalimide Nanosheets: Aggregation-Induced Emission and Unveiling a-PET for Sensitive Detection of Organic Volatile Contaminants in Water, Angew. Chemie. 130 (2018) 8624–8628. https://doi.org/10.1002/ANGE.201802842.

[14] S. Nasiri, P. Palanisamy, M. Rabiei, M. Hosseinnezhad, A. Palevicius, A. Vilkauskas, G. Janusas, V. Nutalapati, Investigation of the influence of persulfurated benzene derivatives on optical and carrier mobility properties, Mater. Lett. 342 (2023) 134323. https://doi.org/10.1016/J.MATLET.2023.134323.

[15] Y. Hong, J.W.Y. Lam, B.Z. Tang, Aggregation-induced emission, Chem. Soc. Rev. 40 (2011) 5361–5388. https://doi.org/10.1039/c1cs15113d.