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Functional Molecules for Organic Light-Emitting Diodes (OLEDs)

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ABSTRACT

Organic optoelectronics is an exciting field that combines chemistry, physics, materials science, and biology to create modern electronic devices that are lightweight, flexible, and cost-effective. One of the most popular applications of this technology is in organic light-emitting diodes (OLEDs), which are widely used in display screens and lighting. This chapter explores the roles of various functional organic molecules in OLEDs, with emphasis on amorphous molecular materials that support uniform thin-film formation. It provides insights into the design and properties of essential components, such as hole- and electron-transporting materials, charge-blocking layers, and emissive materials. Special focus is given to thermally activated delayed fluorescence (TADF) materials, recognised as next-generation emitters due to their high efficiency and metal-free nature. Although remarkable progress has been made, further research is required to enhance OLED device longevity and sustainability. Improvements in organic material design are likely to contribute meaningfully to technological progress and eco-friendly solutions.

Keywords: *Emission Material; Hole and Electron Transporting Material; Optoelectronic Devices; Organic Light-Emitting Diodes*

Introduction

Recently, organic optoelectronics has emerged as a transformative domain at the intersection of materials science, chemistry, and applied physics. This interdisciplinary field focuses on the development of electronic and photonic devices based on organic semiconductors, offering several advantages over traditional inorganic systems. Organic light-emitting diodes (OLEDs), one of the most prominent applications in this field, have revolutionised display and lighting technologies with their thin, lightweight, and flexible structures (Forrest, 2004; Tang & VanSlyke, 1987). Unlike conventional inorganic semiconductors, organic materials can be synthetically tuned at the molecular level to tailor their electronic and optical properties. The structural flexibility of organic molecules enables solution processing, reduced fabrication costs, and

mechanical adaptability—critical attributes for next-generation devices such as foldable displays and wearable electronics (Reineke *et al.*, 2013). OLEDs are notable for their self-emissive nature, high contrast ratios, and capacity to achieve full-colour emissions with low power consumption.

A typical OLED device consists of multiple organic layers, each performing specific functions such as hole and electron transport, charge blocking, and light emission. The selection and design of functional molecular materials for each layer are central to optimising device efficiency and longevity. Amorphous molecular materials are often preferred over crystalline counterparts due to their superior film-forming capabilities and morphological stability (Shirota, 2000).

Recent developments in emitter technology have introduced thermally activated delayed fluorescence (TADF) materials as efficient alternatives to phosphorescent emitters. These third-generation emitters exploit reverse intersystem crossing to harvest both singlet and triplet excitons without requiring heavy metal complexes, thereby enhancing device efficiency while maintaining environmental sustainability (Uoyama *et al*., 2012).

Despite significant advances, challenges such as operational stability, material degradation, and end-of-life recyclability remain. Addressing these issues through molecular engineering and device architecture innovation is essential to fully realise the potential of OLEDs in commercial and sustainable technologies.

This chapter aims to explore the design and application of functional organic molecules in OLEDs, with a special focus on amorphous materials, offering insights into their roles in enhancing device performance and enabling future optoelectronic applications.

Literature Review

Organic light-emitting diodes (OLEDs) have gained significant traction in the realm of display and lighting technologies due to their remarkable attributes, such as thin-film form factors, wide viewing angles, high contrast ratios, and the ability to emit across the visible spectrum (Reineke *et al*., 2013; Tang & VanSlyke, 1987). These devices are now extensively used in smartphones, televisions, smartwatches, and even automotive displays. Their intrinsic flexibility and compatibility with solution processing make them highly suitable for next-generation, flexible, and wearable electronics (Forrest, 2004). A key distinction in the performance of OLED devices lies in the choice of organic materials. Crystalline materials, though known for their superior charge-carrier mobility, often struggle with poor film-forming ability, resulting in grain boundaries that disrupt device uniformity and performance. In contrast, amorphous molecular materials offer better morphological stability, uniform film formation, and compatibility with both vacuum and solution-processing techniques (Shirota, 2000; Friend *et al*., 1999). This has led to their widespread adoption in OLEDs over their crystalline counterparts.

OLED structures generally consist of multiple organic layers performing specialised roles such as hole transport, electron transport, charge blocking, and emission. Materials with appropriate energy levels for hole and electron injection and transport are selected to ensure balanced charge recombination within the emissive layer (Kido, Kimura & Nagai, 1995). Amorphous hole-transport materials such as TCTA and α-NPD (Shirota, Kobata & Noma, 1989) have shown promise due to their stable thin-film characteristics and reversible redox behaviour.

In recent years, research focus has shifted towards third-generation emitters, particularly thermally activated delayed fluorescence (TADF) materials, which enable efficient upconversion of triplet excitons to singlets without relying on expensive noble metals (Uoyama *et al*., 2012). This innovation not only improves internal quantum efficiency but also aligns with sustainability goals.

Furthermore, host materials for emissive dopants must possess high triplet energy levels and balanced bipolar charge-transport properties to ensure effective energy transfer and exciton confinement (Ikai *et al*., 2001). Such careful molecular engineering has been crucial in improving both the efficiency and operational stability of OLED devices.

In summary, the literature reflects a consistent evolution in the molecular design and functional tuning of materials for OLEDs, with amorphous small molecules and TADF compounds at the forefront of current research.

Discussion

Fluorescence or phosphorescence emission is the basis of organic electroluminescence (EL) which originates from the excited singlet or triplet electronic states. These excitons within the device are produced by hole-electron recombination, injected from the anode and cathode, respectively, in presence of an external electrical stimulation.

In case of single-layer devices, the materials should be capable of not only accepting both holes and electrons from the electrodes but also transporting them. In addition, they should have emissive properties, too. It is very difficult to find a single material capable of functioning in various roles. Multiple materials are employed together in the device, where each material is chosen to function as electrode charge injection, transport of charges, preventing charge leakage, and emission of light. Accordingly, they are termed as i) hole-conducting, ii) electron-conducting, iii) charge-blocking, and iv) emissive materials, respectively. Therefore, organic light-emitting diodes are multilayered devices that are normally assembled by vacuum deposition of the individual functional materials.

In general, materials used in OLEDs are expected to have the following characteristics:

1. Formation of uniform thin films with less pinholes is an essential parameter which can be achieved either by thermal deposition under vacuum conditions or by solution-

based processing of the amorphous materials.

2. Material should have a high glass-transition temperature (Tg).

3. High morphological stability.

Amorphous molecular materials are mostly found to be used in OLEDs, as they form smooth, uniform layers compared to crystalline material. The following section of this chapter includes a brief account of amorphous organic compounds used for hole and electron transport, hole and electron blocking, and light emission.

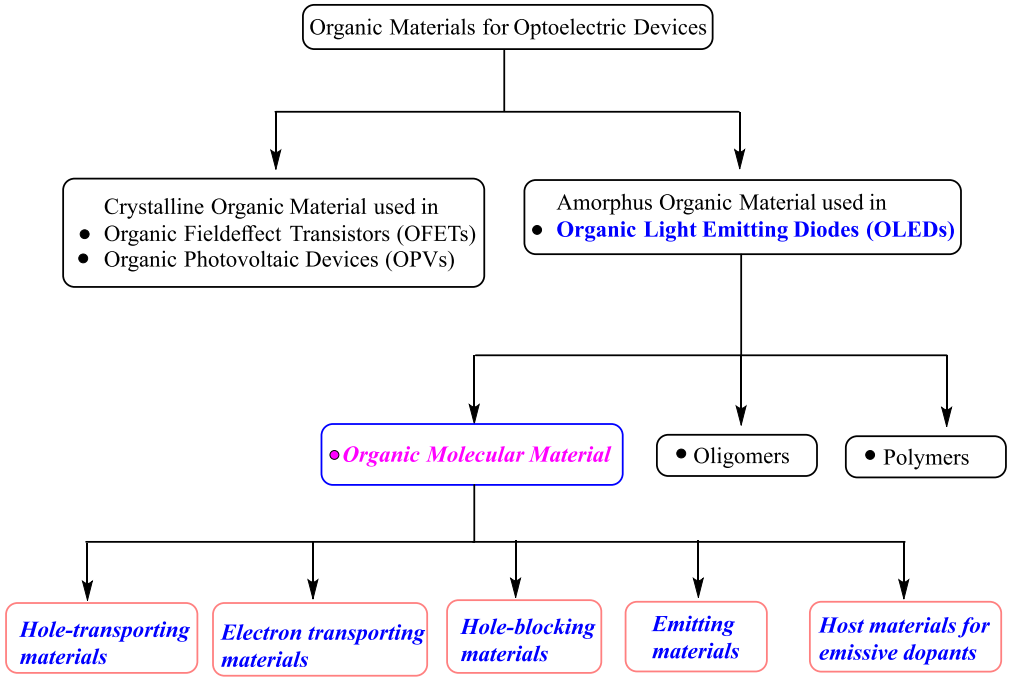

Figure 1: Classification of Organic Compounds Utilised in Optoelectronic Devices

Hole Transporting Materials

Materials used for hole transport should possess appropriate HOMO energy levels to accept the cation-radical species (hole carriers) from the anode through the hole-injection layer, indicating the reversibility of their anodic oxidation process. Organic molecules with low ionisation potential are mainly selected as hole-transporting components in the hole-injection layer. A variety of under this category have been reported to date and few representative examples include 4,4',4"-tris(3-methylphenyl(phenyl)amino)triphenylamine(m-MTDATA) 1 (Shirota, Kobata & Noma, 1989), 4,4',4"-tri-N-carbazolyltriphenylamine (TCTA) 2 (Kuwabara *et al*., 1994) and *α*-NPD3 (Van Slyke, Chen & Tang, 1996), as illustrated in figure 2. Interestingly, m-MTDATA 1 is primarily employed as a hole injection materials whereas TCTA 2 and *α*-NPD 3 are the widely utilised amorphous molecular materials for hole transport in OLEDs.

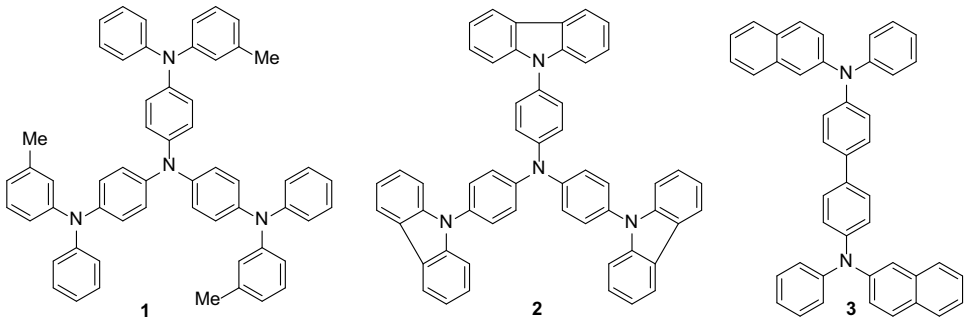

Figure 2: Amorphous Organic Compounds Utilised in Hole Transport

Electron-transporting Materials

In a similar way, materials used for electron transport should possess suitable LUMO energy levels to receive the anion-radical species (electron carriers) from the cathode via the electron-injection layer, reflecting the reversible nature of their cathodic reduction processes. Organic molecules in this category consist of central aromatic cores like benzene,1,3,5-triazine,1,3,5-triphenylbenzene and tetraphenylmethane, to which electron-accepting groups like pyridine, oxadiazole, triazine, triarylborane and dimesitylboryl are connected. In this direction, few examples of electron transporting materials are presented in figure 3 (Gao *et al.*, 1999; Noda & Shirota, 1998; Sasabe & Kido, 2011).

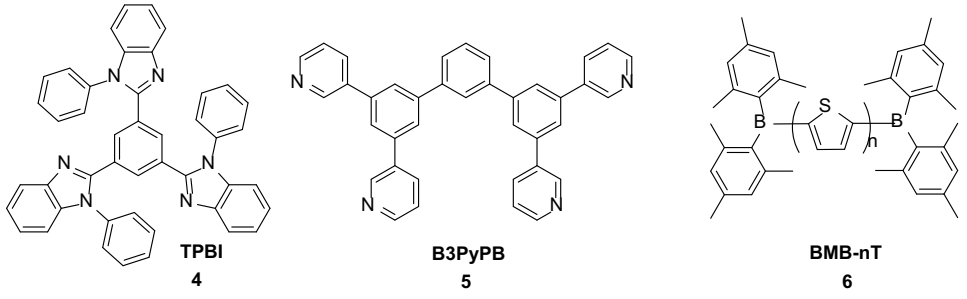

Figure 3: Amorphous Organic Compounds for Electron Transport

Hole-blocking Materials

These materials are used to develop charge blocking layers that trap both types of charge carriers within the emitting layer by effectively preventing leakage of charge from the emitting layer. Interestingly, hole-transporting materials are used to block electron charge carriers, whereas electron-transporting materials are naturally used in hole-blocking. Materials in this category should have high ionisation potential, which is essential to resist the uptake of hole carriers releasing from the emitting layer.

Emitting Materials

Molecule used as emitting materials should exhibit a bipolar characteristic in which

HOMO and LUMO energy levels are aligned in such a way that they can allow the acceptance of holes from the anode and electrons from the cathode. Emitting layer behaves like a recombination centre for holes and electrons. In this direction, it is important to mention that the stability of the charge carriers (both cation-radical and anion-radical) in emitting molecules is another critical parameter for the functioning of the emitting layer as a recombination centre.

Fluorescence-emitting Materials

Compounds BMA-nT 7 and FlAMB-nT 8 are used in OLED applications as bipolar amorphous molecular emitters (Figure 4). The emission colour depends on the extent of conjugation associated with the oligothiophene segment in BMA-nT (Noda *et al*., 1997) and FlAMB-nT (Shirota *et al*., 2000).

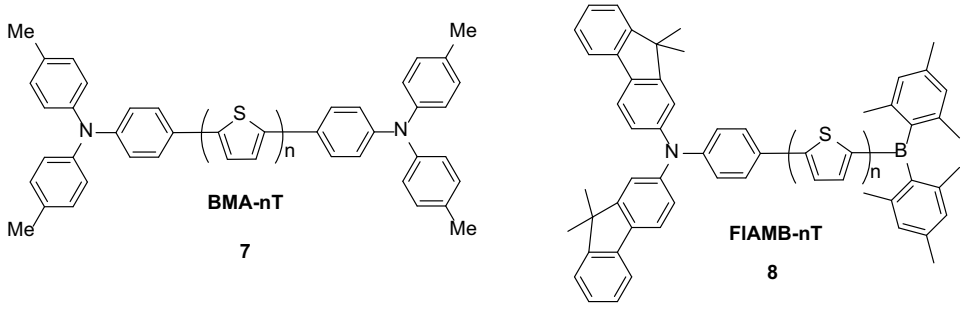

Figure 4: Bipolar-emitting Amorphous Molecular Materials

Thermally Assisted Delayed Fluorescence-Emitting Materials

TADF, or thermally activated delayed fluorescence, is produced by thermal up conversion of triplet to singlet exciton and is used in fluorescence-based OLEDs having high performance. TADF-emitting materials are superior compared to the phosphorescent dopant materials, as the former material does not contain any expensive transition metals. For this reason, TADF materials are referred to as third-generation emitters in OLED technology. In general, TADF emitting materials have a large extent of spin-orbit coupling and a slight energy gap between singlet-triplet states to promote intersystem crossing in the reverse direction.

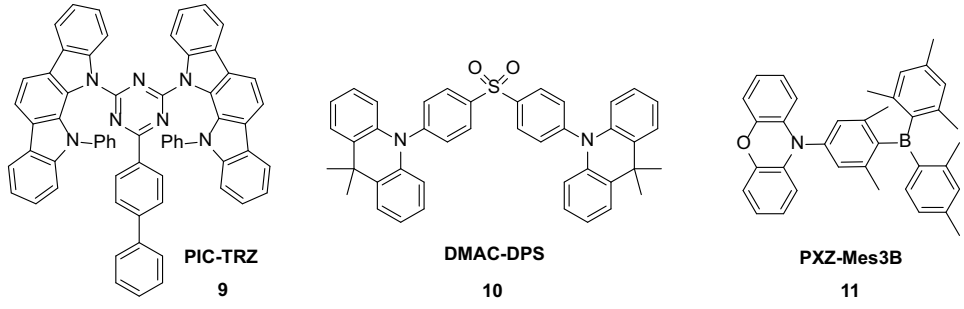

Figure 5: TADF-emitting Molecular Materials

It has been found that the reported TADF molecules possess carbazole, acridan or phenoxazine segments as electron donors and triazine (Endo *et al*., 2011), triaryl boron (Suzuki *et al*., 2015), diphenyl sulfone (Zhang *et al*., 2014), or diphenylketone segments as electron acceptors. Amalgamation of electron donating and accepting moieties in TADF molecules is very important, as it facilitates intramolecular charge transfer. Few examples of synthesised TADF materials are given in figure 5.

Phosphorescence-emitting Materials

Transition metal complexes of platinum, iridium and osmium are usually used in OLEDs as room-temperature phosphorescent materials (figure 6) (Baldo *et al.*, 1999). These complexes are used as emissive dopants with a good film-forming host material, as metal complexes lack the ability to form films. However, the colour of the emissions depends on the structure of the ligands.

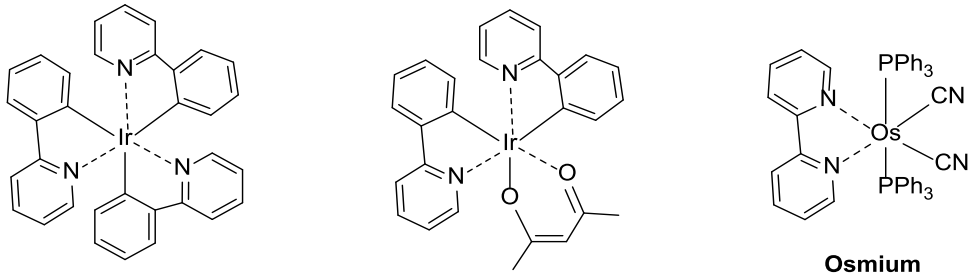

Figure 6: Phosphorescent Dopants for OLEDs

Host Material for Emmisive Dopant

Emissive dopant materials used in OLEDs usually need host materials having good film-forming ability. The role of the host material is to generate excitons and then transfer the excitation energy to emissive dopant materials via the singlet-singlet or triplet-triplet process. The host materials possess a bipolar character to accept both types of charge carriers, and energy levels of singlet and triplet excited states should exceed that of emissive dopants to transfer exothermic energy efficiently. Transfer of energy in reverse direction, i.e., from dopant to the host, is energetically unfavourable. Some examples of such material are given in Figure 7 (Ikai *et al.*, 2001).

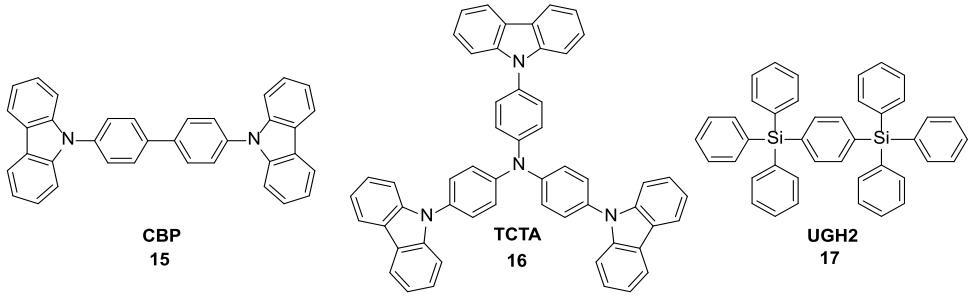

Figure 7: Examples of Materials for Emissive Dopants

Conclusion

This chapter has provided a brief account of the recent advancement in the field of organic optoelectronics, with a focus on the use of molecular organic amorphous materials in OLEDs. Several classes of organic molecular materials used in OLEDs to facilitate acceptance of charge from electrodes, charge blocking, charge transport, and emission were discussed along with the examples of each type. Discussion on the TADF materials as the third-generation OLED emitters has also been included in this chapter. Oligomers and polymer-based organic materials are not considered here despite having their roles in OLEDs.

Even though several types of organic molecular materials have been made targeting to improve external quantum efficiency for OLEDs, further improvements are still required for getting a better lifespan of OLED displays and lighting panels and to develop recycling and disposal methods for OLED devices. Research and development in functional organic material synthesis may reduce the production costs for OLEDs, which can make OLED technology more accessible to a broader range of consumers. OLEDs could have been integrated with other emerging technologies to solve the environmental and energy challenges of the 21st century.

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References

Baldo, M. A., Lamansky, S., Burrows, P. E., Thompson, M. E., & Forrest, S. R. (1999). Very high-efficiency green organic light-emitting devices based on electrophosphorescence. *Applied Physics Letters, 75*(1), 4–6. https://doi.org/10.1063/1.124258

Endo, A., Sato, K., Yoshimura, K., Kai, T., Kawada, A., Miyazaki, H., & Adachi, C. (2011). Efficient up-conversion of triplet excitons into a singlet state and its application for organic light emitting diodes. *Applied Physics Letters, 98*(8). https://doi.org/10.1063/ 1.3558906

Forrest, S. R. (2004). The path to ubiquitous and low-cost organic electronic appliances on plastic. *Nature, 428*(6986), 911-918. https://doi.org/10.1038/nature02498

Friend, R. H., Gymer, R. W., Holmes, A. B., Burroughes, J. H., Marks, R. N., Taliani, C. D. D. C., ... & Salaneck, W. R. (1999). Electroluminescence in conjugated polymers. *Nature, 397*(6715), 121-128. https://doi.org/10.1038/16393

Gao, Z., Lee, C. S., Bello, I., Lee, S. T., Chen, R. M., Luh, T. Y., ... & Tang, C. W. (1999). Bright-blue electroluminescence from a silyl-substituted ter-(phenylene–vinylene) derivative. *Applied Physics Letters, 74*(6), 865-867. https://doi.org/10.1063/1.123392

Ikai, M., Tokito, S., Sakamoto, Y., Suzuki, T., & Taga, Y. (2001). Highly efficient phosphorescence from organic light-emitting devices with an exciton-block layer. *Applied Physics Letters, 79*(2), 156–158. https://doi.org/10.1063/1.1385182

Kido, J., Kimura, M., & Nagai, K. (1995). Multilayer white light-emitting organic electroluminescent device. *Science, 267*(5202), 1332-1334. https://doi.org/10.1126/science.267.5202.1332

Kuwabara, Y., Ogawa, H., Inada, H., Noma, N., & Shirota, Y. (1994). Thermally stable multilayered organic electroluminescent devices using novel starburst molecules, 4,4′,4″-tri(N-carbazolyl)triphenylamine (TCTA) and 4,4′,4″-tris(3-ethylphenylphenylamino) triphenylamine (m-MTDATA), as hole-transport materials. *Advanced Materials, 6*(9), 677–679. https://doi.org/10.1002/adma.19940060913

Noda, T., & Shirota, Y. (1998). 5,5′-Bis(dimesitylboryl)-2,2′-bithiophene and 5,5″-bis(dimesitylboryl)-2,2′:5′,2″-terthiophene as a novel family of electron-transporting amorphous molecular materials. *Journal of the American Chemical Society, 120*(37), 9714–9715. https://doi.org/10.1021/ja9817343

Noda, T., Imae, I., Noma, N., & Shirota, Y. (1997). 5,5″-Bis{4-[bis(4-ethylphenyl) amino]phenyl}-2,2′:5′,2″-terthiophene and 5,5‴-bis{4-[bis(4-methylphenyl)amino]phenyl}-2,2′:5′,2″:5″,2‴-quaterthiophene as a novel family of amorphous molecular materials. *Advanced Materials, 9*(3), 239–241. https://doi.org/10.1002/adma.19970090311

Reineke, S., Thomschke, M., Lüssem, B., & Leo, K. (2013). White organic light-emitting diodes: Status and perspective. *Reviews of Modern Physics, 85*(3), 1245-1293. https://doi.org/10.1103/RevModPhys.85.1245

Sasabe, H., & Kido, J. (2011). Multifunctional materials in high-performance OLEDs: Challenges for solid-state lighting. *Chemistry of Materials, 23*(3), 621–630. https://doi.org/10.1021/cm1024052

Shirota, Y. (2000). Organic materials for electronic and optoelectronic devicesBasis of a presentation given at Materials Chemistry Discussion No. 2, 13–15 September 1999, University of Nottingham, UK. *Journal of Materials Chemistry, 10*(1), 1-25. https://doi.org/10.1039/A908130E

Shirota, Y., Kinoshita, M., Noda, T., Okumoto, K., & Ohara, T. (2000). A novel class of emitting amorphous molecular materials as bipolar radical formants: 2-{4-[Bis (4-methylphenyl) amino] phenyl}-5-(dimesitylboryl) thiophene and 2-{4-[Bis (9, 9-dimethylfluorenyl) amino] phenyl}-5-(dimesitylboryl) thiophene. *Journal of the American Chemical Society, 122*(44), 11021-11022. https://doi.org/10.1021/ja0023332

Shirota, Y., Kobata, T., & Noma, N. (1989). Starburst molecules for amorphous molecular materials. 4, 4', 4"-Tris (N, N-diphenylamino) triphenylamine and 4, 4', 4"-tris [N-(3-methylphenyl)-N-phenylamino] triphenylamine. *Chemistry Letters, (7)*, 1145-1148. https://doi.org/10.1246/cl.1989.1145

Suzuki, K., Kubo, S., Shizu, K., Fukushima, T., Wakamiya, A., Murata, Y., Adachi, C., & Kaji, H.

(2015). Triarylboron-based fluorescent organic light-emitting diodes with external quantum efficiencies exceeding 20%. *Angewandte Chemie International Edition, 54*(50), 15231–15235. https://doi.org/10.1002/anie.201508270

Tang, C. W., & VanSlyke, S. A. (1987). Organic electroluminescent diodes. *Applied Physics Letters, 51*(12), 913-915. https://doi.org/10.1063/1.98799

Uoyama, H., Goushi, K., Shizu, K., Nomura, H., & Adachi, C. (2012). Highly efficient organic light-emitting diodes from delayed fluorescence. *Nature, 492*(7428), 234–238. https://doi.org/10.1038/nature11687

Van Slyke, S. A., Chen, C. H., & Tang, C. W. (1996). Organic electroluminescent devices with improved stability. *Applied Physics Letters, 69*(15), 2160–2162. https://doi.org/10.1063/1.117151

Zhang, Q., Li, B., Huang, S., Nomura, H., Tanaka, H., & Adachi, C. (2014). Efficient blue organic light-emitting diodes employing thermally activated delayed fluorescence. *Nature Photonics, 8*(4), 326–332. https://doi.org/10.1038/nphoton.2014.12