

Crystallography-Assisted OLED Materials Development

Manju Rajeswaran

Kodak Research Laboratories
Eastman Kodak Company
1999 Lake Avenue, Rochester, NY, USA, 14650-2106
manju.rajeswaran@kodak.com

Abstract: *Materials science plays a crucial role in the efficiency, color, and lifetime performances of Organic Light-Emitting Diode devices (OLEDs). Whether the device emits red, green, blue, or white light, each color system requires a complex set of organic or organometallic materials such as hosts, dopants, and transport materials. For the majority of materials that are crystalline in the solid state, their structure is a key feature in the control of their chemical and physical properties and hence their OLED performance. Chemical crystallography provides detailed molecular structure in a way that no other science can begin to approach. OLED chemistry is solid-state chemistry for which crystallography provides the maximum possible information—a complete picture. The role of crystallography in OLED materials development at Eastman Kodak Company includes the establishment of synthetic pathways, impurity identification, elucidation of stoichiometry and chemical composition, isomer and polymorph identification, and the determination of conformational and molecular structure affecting the reactivity, hue, and stability of the materials.*

Keywords: OLED; white OLEDs; yellow dopant; crystallography; tetracene; rubrene; DBzR

Introduction

Display technologies based on OLEDs are rapidly emerging as powerful info imaging vehicles. Recent growth of OLED technology is largely attributed to the advantages that they offer, viz., full-color displays that can be viewed at wide viewing angles and low power requirements. Besides device architecture, materials science also plays a crucial role in the efficiency, color, and lifetime performances of OLED devices. Whether the device emits red, green, blue, or white light, each color system requires a complex set of organic or organometallic materials providing hosts, dopants, and transport materials. For the majority of materials that are crystalline in their solid state, the structure is a key feature in the control of their chemical and physical properties. Chemical crystallography provides detailed molecular structure in a way that no other science can begin to approach. The role of crystallography in OLED materials development at Kodak is presented here, using a yellow dopant (YD) as an example.

OLED display technology has seen significant commercial growth since it was first reported by Tang and Van Slyke [1] with full-color active-matrix OLED (AMOLED) displays now commercialized [2–3]. Manufacturing yield and cost issues have prompted us to

consider the use of white OLEDs (figure 1) with color filters as a preferred method of manufacturing large area displays.

Rubrene (figure 2) is an electroluminescent material that is well known in the chemical literature and, in recent years, has been used as a yellow-light-emitting material or dopant in OLED devices. When combined with a blue-light-emitting dopant, rubrene can be used for the production of white OLEDs. However, for the successful manufacture of such devices, dopants must exhibit good stability and efficiency. It has been found that the stability and performance of the rubrene-based yellow-light-emitting component can be controlled by careful substituent selection. An example of such a rubrene-based derivative is DBzR (figure 3), which was the yellow dopant of choice in the industry in early 2004.

Cathode (LiF/Aluminum)
Electron-transporting layer
Blue-emitting layer
Yellow-orange emitting layer
Hole-transporting layer
Hole-injection layer
Anode (ITO)
Substrate

Figure 1. White OLED

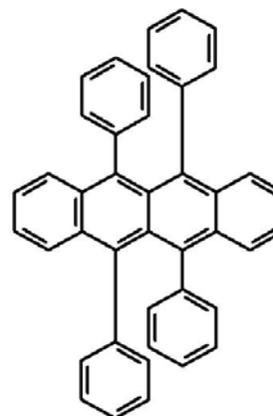


Figure 2. Rubrene

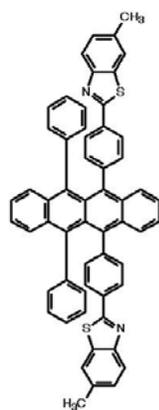


Figure 3. DBzR

However, there are problems associated with DBzR:

1. High sublimation temperature (>330°C);
2. Thermal decomposition; and
3. Degradation components are non-yellow emitting.

Because of these thermal stability issues, there was an urgent need to develop a more stable replacement. Requirements for the new dopant were:

1. Lower sublimation temperature (<330°C);
2. Retained or improved DBzR-like performance; and
3. Improved thermal stability, thus eliminating, or at the very least minimizing, degradation over a prolonged sublimation period.

Results and Discussion

Development of a new yellow dopant necessitated a synthetic route, which could provide ready access to carefully selected substituted rubrenes. A literature search revealed an old synthetic route to rubrene [4] (figure 4) with development potential. However, initial experiments resulted in isomer formation.

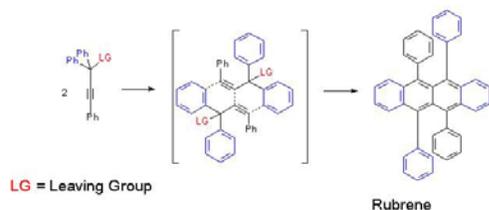


Figure 4: Rubrene synthesis from literature

In an effort to understand the reaction mechanism, a reaction intermediate was isolated and identified by single crystal x-ray diffraction as having an allene structure, (figure 5). In addition, an impurity from a separate reaction mixture was isolated and its structure again by x-ray diffraction, identified as a cyclobutene derivative, (figure 6). These materials lead us to believe that the rubrene derivatives are formed via a double [2+4] cycloaddition reaction with elimination of HCl whereas; the cyclobutene impurity is formed via a [2+2] cycloaddition reaction, (figure 7). Knowing the reaction mechanism, a series of substituted rubrenes, free of isomers, was successfully synthesized and tested in

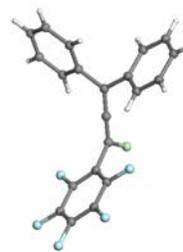


Figure 5. Allene



Figure 6. Impurity

devices. Of these materials, several were identified as having luminance characteristics similar to or better than DBzR. Figure 8 illustrates a comparison chart for the thermal stability of one such dopant, YD, and its comparison to DBzR. These materials on exposure to air and light lose their color. The crystal structure of the photooxidation product (figure 9), revealed it to be an endoperoxide. Before sublimation, YD is bright yellow in color, whereas during and after sublimation, it turns bright orange-red (figure 10). Crystal structures of these samples revealed that both were different polymorphs of the same material (figure 11). As seen from the crystal structure in figure 12, the naphthalene nucleus of the yellow polymorph of YD is flat, whereas that of the orange polymorph is twisted. It was established that this orange polymorph was more prone to photo-oxidation and hence less stable than the yellow form (figure 13). Comparing the packing patterns of the two polymorphs (figure 14), one can easily see that packing of the tetracene units in the yellow form is more compact and thus less exposed to reaction.

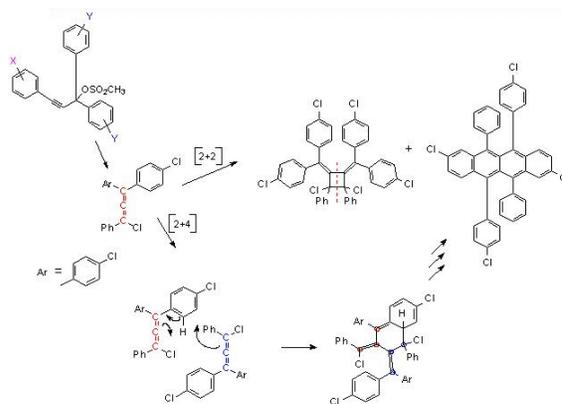


Figure 7. Mechanism of reaction

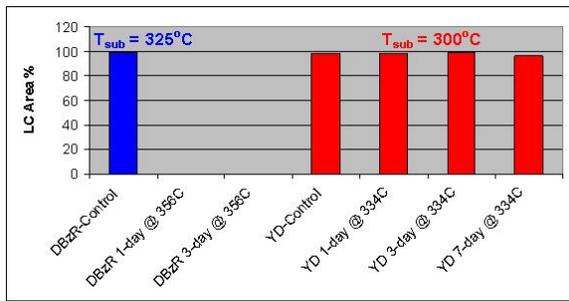
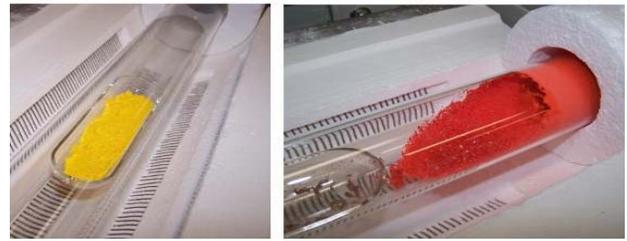


Figure 8. Thermal stability comparison, YD vs. DBzR



(a) (b)

Figure 10. Sublimation, (a) before, and (b) after

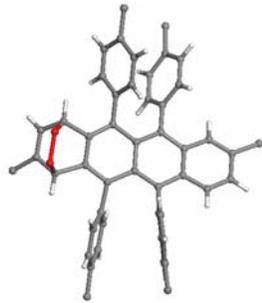


Figure 9. Endoperoxide

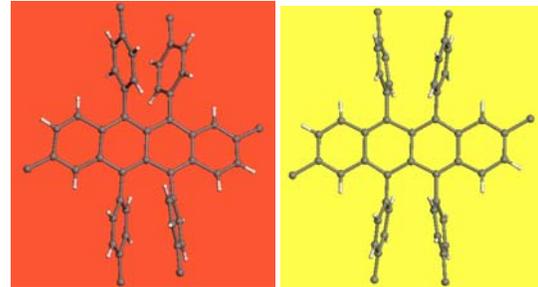


Figure 11. YD polymorphs

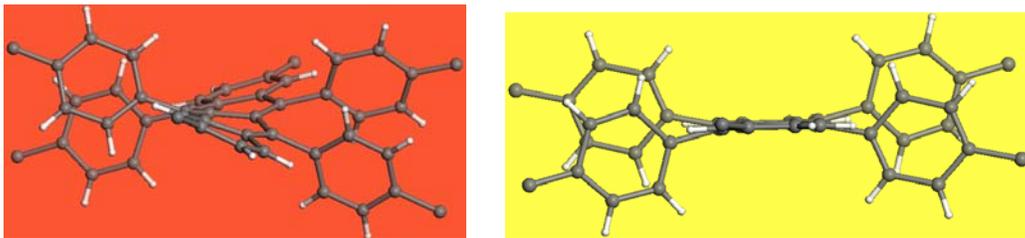


Figure 12. Twisted vs. flat crystal structures of YD

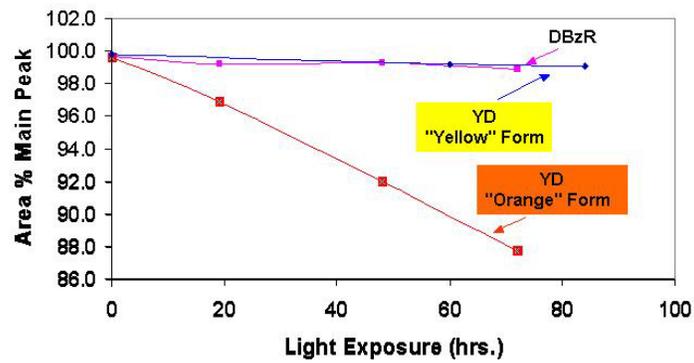


Figure 13. Solid state endoperoxide formation

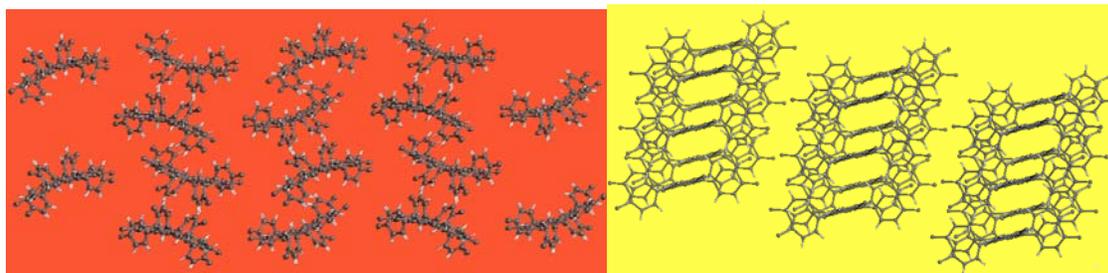


Figure 14. Crystal packing comparison for two polymorphs of YD

Conclusions

Looking at these results, one can see that crystallography was used with a good deal of success in the development of a yellow dopant by:

1. Establishing a successful synthetic pathway;
2. Identification of reaction impurities;
3. Establishment of the stoichiometry and chemical composition of newly synthesized materials;
4. Isomer and polymorph identification; and
5. Studying the effect of conformation and molecular structure on device performance of new materials.

There are several other ways that are not very obvious from the above example, in which crystallography has been essential for OLED materials development, to name a few:

1. Characterizing crystals formation during development, scale up, and/or manufacturing stages;
2. Designing new materials with specific properties;
3. Crystal structures can form the basis for molecular modeling studies, which improve the understanding of intermolecular interactions; and
4. Crystallography is needed (directly or indirectly) for the identification of starting materials and end products in devices.

Because the operation of OLED devices involves the chemistry of materials in the solid state, the importance

of crystallography to OLED cannot be underestimated. Simply put, it has the potential to allow us to get a better understanding of the chemistry occurring in the device and to design more efficient and better performing OLED materials.

Acknowledgments

The author wishes to thank Dr. William J. Begley, project leader, synthetic chemist, and “the brains” for this project, for his leadership and encouragement.

References

1. Tang, C. W., and S. A. Van Slyke, *Appl. Phys. Lett.* vol. 51, p. 913, 1987.
2. Rajeswaran, G., M. Itoh, M. Boroson, S. Barry, T. K. Hatwar, K. Kahen, K. Yoneda, N. Komiya, H. Kanno, and H. Takahashi, *SID '00 Digest*, p. 974, 2000.
3. Hatwar, T. K., J. P. Spindler, M. L. Ricks, R. H. Young, Y. Hamada, N. Saito, K. Mameno, R. Nishikawa, H. Takahashi, and G. Rajeswaran, *SPIE*, vol. 5214, p. 233, 2003.
4. Moureu, C., C. Dufraisse, et al., *Compt. Rend. Acad. Sci.*, vol. 183, p. 685, 1926; Essenfeld, A. P., US Patent 4,855,520.