

# Studies on Excited/States Dynamics for Organic Long/Persistent Luminescence Materials

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<https://doi.org/10.15017/4060117>

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出版情報 : 九州大学, 2019, 博士 (工学), 課程博士  
バージョン :  
権利関係 :

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論 文 名 : Studies on Excited-States Dynamics for Organic Long-Persistent Luminescence Materials

(有機蓄光の励起状態挙動に関する研究)

区 分 : 甲

### 論 文 内 容 の 要 旨

Realizing long persistent luminescence (LPL) from organic systems as well as inorganic LPL materials at room temperature is an important issue to solve the materials, sustainability. In 2017, Kabe and Adachi realized the first organic long persistent luminescence (OLPL) material using the organic donor/acceptor binary system (TMB/PPT), which also has the power-law emission kinetics like inorganic materials and far beyond the emission duration of all existing organic room-temperature phosphorescence systems. However, such a small molecule system has poor mechanical properties and LPL performance that does not meet the requirements of commercial LPL materials, even though it possesses high transparency that is difficult to achieve with inorganic materials. In this thesis, for the development of multicolor, long duration, and flexible OLPL system, the color-tuning and the excited-state dynamics of LPL and were studied. Moreover, the first flexible and transparent polymer-based OLPL system was realized.

In **Chapter 1**, the definition and historical backgrounds of LPL are described. The differences between LPL and phosphorescence are clarified. The advantages and issues of OLPL materials are illustrated.

In **Chapter 2**, an orange donor/acceptor binary OLPL system was demonstrated by replacing TMB with a low HOMO level donor. I found a donor TTPD, which is easier to chemically modify than TMB, exhibits a similar HOMO level to TMB. Then, the lower HOMO donor TBAPD was synthesized by electron-donating substitutions into TTPD. The emission spectra of a TBAPD/PPT film shifted to the orange range and its LPL continued for approximately 5 minutes. This work proved LPL spectra can still be tuned by adjusting the HOMO level of donors.

In **Chapter 3**, the influence of charge-transfer and local excited states' energy gap,  $\Delta E(^1CT-^3LE_D)$ , in exciplex system on OLPL was demonstrated by comparing the transient PL spectra in different time-ranges and LPL performance of three donors possessing similar molecular structures but different HOMO and triplet energy levels. The OLPL efficiency was reduced along with decreasing the energy level of  $^3LE_D$  which is lower than that of the  $^1CT$ , because a large  $\Delta E(^1CT-^3LE_D)$  encourages a larger population of triplet Frenkel excitons. These excitons on  $^3LE_D$  are difficult not only to re-convert into charge-transfer excitons but also to divide into separated radical ion pairs. They released the exciting energy by the phosphorescence of donors, which induces the dual emission from both  $^1CT$  and  $^3LE_D$ . Especially, the TTB/PPT system showed a white light without the use of additional dopants. Moreover, the LPL emission spectra were also affected by the absorption of the donor radical cations generated by the charge separation process. This work provided a foundation for designing efficient OLPL systems using both small molecules and polymers.

In **Chapter 4**, the first polymer-based OLPL system was achieved by blending the low-concentration TMB into an acceptor polymer, PBPO. Hinging on the high mechanical performance of PBPO, this polymer-based OLPL system exhibits excellent flexibility and the thick film can be bent without making cracks. However, because of the large  $\Delta E(^1CT-^3LE_D)$ , conspicuous phosphorescence of TMB was observed for the first ten seconds after excitation. The subsequent LPL also contained the phosphorescence component. The outstanding flexibility and high transparency of this polymer-based OLPL film clearly demonstrated the superiority of polymer-based OLPL systems to polymer composites compounded with inorganic LPL powders.

The works in this thesis will guide the design of new OLPL systems in the future.