Bright organic long persistent luminescence by improving carrier accumulation and emission processes

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（電荷蓄積過程および発光過程の改善による
高輝度有機蓄光材料の開発）

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論　文　内　容　の　要　旨

In **Chapter 1**, the background and motivation of this thesis are introduced. Long persistent luminescent (LPL) materials have applications in glow-in-the-dark paints such as emergency signs and watches. Current highly efficient LPL materials are based on inorganic materials. In contrast, Kabe and Adachi recently developed a novel LPL emitter composed only of organic molecules. The first organic LPL (OLPL) system consists of a small amount of electron donor molecule, TMB, and a large amount of acceptor molecule, PPT. The absorbed light energy is accumulated in a charge separated (CS) state between the donor and the acceptor. After that, the separated carriers slowly recombine and exhibit a charge transfer (CT) emission for a long time. Therefore, the OLPL mechanism can be separated into the carrier accumulation process and emission process.

The OLPL system has many advantages over inorganic LPL materials in solubility, transparency, and flexibility. However, the first OLPL system has a much shorter emission duration than that of inorganic LPL materials. A fabrication method of the OLPL systems is limited to a melt-cast method, and only green LPL emission color has been reported. In this thesis, I proposed novel OLPL systems by improving both carrier accumulation and emission processes.

In **Chapter 2**, the transparent OLPL films were fabricated by a solution process and a thermal evaporation process instead of a melt-cast process. A donor molecule *m*-MTDATA was used instead of TMB because TMB is unstable to heat and solvents. Although both of TMB/PPT and *m*-MTDATA/PPT films exhibited similar emission spectra, the LPL duration of *m*-MTDATA/PPT was longer than that of TMB/PPT because of the higher Φ_{PL} of *m*-MTDATA/PPT. Moreover, the high quality and smooth films were achieved by thermal evaporation and spin-coating method because of the high stability of *m*-MTDATA. This work demonstrated the high processability of OLPL systems and the relation between the Φ_{PL} and LPL duration.

In **Chapter 3**, several fluorescent molecules were doped into the OLPL system for

improving the Φ_{PL} and tuning the emission color of the OLPL. The first OLPL system exhibits only green emissions with a short duration because its emission originates from CT between the HOMO of the donor and the LUMO of the acceptor. These problems were resolved by adding a small amount of fluorescent dopant into the CT matrix. The fluorescent molecules harvest the excitons on the CT excited stated through Förster energy transfer, and the fluorescent dopants produce efficient emission with improved color purity. Therefore, the LPL emission color was controlled by the fluorescent molecules from greenish blue to red and even white. At the same time, the LPL duration was enhanced because of the improvement of the Φ_{PL}. Moreover, some fluorescent dopants trapped electrons and extended the LPL durations because the dopants have a deeper LUMO level than that of the acceptor, PPT. This work demonstrated that doping fluorescent molecules improved not only the emission process but also the carrier accumulation process.

In **Chapter 4**, a novel p-type OLPL system, which can work even in the air was developed. The reported OLPL systems can be considered as an n-type OLPL system because the donor concentration is low and only radical anions can diffuse through acceptor molecules. However, radical anions can easily react with oxygen and impurities. To improve material selectivity and stability, developing a p-type OLPL system, in which radical cations diffuse is required. A cationic organic photoredox catalysts were used as the acceptor since the cationic acceptors form neutral radicals in the CS state. The deep HOMO and LUMO levels of the cationic acceptors and the formation of the neutral radical in the CS state prevent reaction with oxygen. Moreover, the doping of hole-trapping materials improved the carrier accumulation process and exhibited the longest LPL duration. This work demonstrated p-type OLPL systems can improve the several properties of OLPL systems and will contribute great development of OLPL systems in the future.

In **Chapter 5**, the summary of this thesis and prospects are described.

〔作成要領〕

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