Triplet exciton management towards electrically driven organic lasers

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論 文 名：Triplet exciton management towards electrically driven organic lasers
（電流注入型有機半導体レーザーの高性能化のための三重項励起状態の制御）

区　分　：甲

論　文　内　容　の　要　旨

Quenching of singlets by long-lived triplets, namely singlet-triplet annihilation (STA), and a decrease of singlet exciton population density are serious issues for continuous-wave (CW) operation of organic lasers. As a strategy to scavenge or manage unnecessary triplets, an organic laser dye has been dispersed into a triplet-scavenging material having high singlet and low triplet energy levels to remove dye's triplets and keep dye's singlets intact. However, previously reported small molecular triplet scavengers are easily crystallized at higher concentrations or the gas state (for example, oxygen), thereby limiting their usage as the host material. Thus, molecules, which can be used as both triplet-scavenging and host materials, have extremely been limited. Hence, in this thesis, I focused on constructing a triplet scavenging guest-host system having a unique lasing material of 2,6-dicyano-1,1-diphenyl-$\lambda^5\sigma^4$-phosphinine (DCNP) with the aim of efficient and stable lasing.

In **Chapter 1**, I described the definition, historical backgrounds, potential advantages, and future applications of organic lasers. The research problem inhibiting CW optical operation and current injection organic semiconductor laser diodes (OSLDs) is identified. To resolve triplet accumulation which is one of the major issues of organic lasers, I proposed to introduce an efficient triplet scavenging using a host material.

In **Chapter 2**, I synthesized an organic laser dye, DCNP having a small singlet-triplet energy gap of 0.44 eV, and I used 4-4′-bis[(*N*-carbazole)styryl]biphenyl (BSBCz) as the triplet scavenging host for DCNP, i.e., the triplets formed on DCNP are easily transferred to BSBCz. I discussed optical properties of this guest-host matrix and experimentally evaluated in detail with the extensive photophysical assessment such as triplet scavenging capability and rate of exciton transitions. Then, I compared photoluminescence quantum yield and amplified spontaneous emission threshold with the variation of DCNP doping concentration in BSBCz. A 1 wt.%-DCNP-doped BSBCz film, which was formed on top of a mixed-order distributed feedback (DFB) grating, showed lasing with a low threshold value of ~0.86 μJ cm^{-2} and a full-width-at-half-maximum value of ~0.5 nm. Owing to the suppressed triplet accumulation in this system, I succeeded to demonstrate lasing under true-CW operation, with a low threshold of 72 W cm^{-2} and a long CW-laser half-lifetime of ~3 min at a 3.6 kW cm^{-2} excitation power. Furthermore, I verified laser emission by plane polarized light output, far-field beam interference, decay

lifetime of excitons, and visible beam observed on an illuminance paper. In addition, I compared suppression of STA at long pulsed optical excitation with conventional host material.

In **Chapter 3**, based on the excellent optical properties of the DCNP:BSBCz system, I extended the experiment to evaluate electrical and electroluminescence (EL) properties. I optimized single layer based organic light emitting diodes (OLEDs) for obtaining perfect charge balance, and three types of OLEDs were compared to clarify the triplet scavenging capability of BSBCz as a host material. Even though 75 % triplet excitons were generated under electrical excitation, optimized devices with the 1 wt.%-DCNP:BSBCz emissive layer exhibited the complete suppression of efficiency roll-off at high current densities. Additionally, transient EL results revealed the complete suppression of EL-STA even under the condition of 1 ms long pulses at a high current density of 10 A cm^{-2}.

In fact, this unique guest-host system is promising for current injection OSLDs, I explained ongoing experiments in **Chapter 4** with devices having an OLED architecture combined with a DFB optical resonator. Then, I discussed prospects of efficient and practical OSLDs in two different approaches. In addition, I discussed future aspects of different triplet management methods briefly. The results obtained in this thesis paved a promising pathway to imminent demonstration of future OSLDs.

Finally, I discussed fundamentals of DFB lasers in **Appendix A**, to simply clarify optical physics behind DFB optical resonators, and its usage for integrated organic lasers.