有機発光ダイオード、有機発光トランジスター，有機レーザーの現状と将来

Organic LED, Light-emitting FET and Organic LD-present status and outlook-

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We report recent progresses on organic light emitting devices such as organic light emitting diode (OLED), light-emitting organic field effect transistor (LE-OFET) and organic laser diode (OLD). We demonstrate very low driving voltage of OLEDs using a p-i-n structure which also provides high current carrier injection over kA/cm^2. Further we demonstrate novel organic devices such as light emitting FET. We also discuss future prospect of OLD based on our recent materials' development and analysis of operation mechanism.

I. ORGANIC LIGHT EMITTING DIODE

Organic light-emitting diodes (OLEDs) (**FIG1**) have being developed intensively as alternative light sources to inorganic LEDs by taking into advantage of high-efficiency RGB emissions, low-temperature processability, and flexibility. Although OLEDs have such kinds of advantages, the driving voltages are much higher than those for inorganic LEDs. Therefore, lowering driving voltages is crucially important to improve power conversion efficiencies and lifetime issues. To solve the driving voltage problem, OLEDs with *p*-doped hole transport and *n*-doped electron transport layers, called *p-i-n* OLEDs, have been emerging as low-voltage efficient light sources. Lowered driving voltages in *p-i-n* OLEDs are derived from factors including: (1) Charge transfer from matrix to dopant molecules induces generation of free charge carriers, leading to high electrical conductivities in these layers; (2) Generated carriers fill deep carrier traps and deep states in the density-of-states distribution in a disordered carrier hopping system, enhancing effective carrier mobilities; (3) Doping of transport layers induces Fermi level shift, leading to efficient carrier tunnel injection across metal/organic interfaces, i.e., ohmic contacts.

In addition to improvement in OLED characteristics, *p-i-n* OLED structures will open the way to achieving electrically pumped organic laser diodes (OLDs). *p-i-n* OLEDs with low 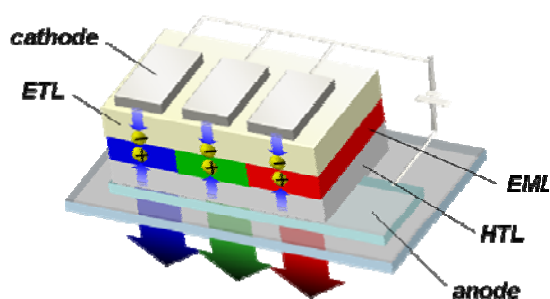driving voltages would make attaining high threshold current densities on the order of 4 kA/cm^2 under electrical pumping possible, which was calculated from a threshold energy under optical pumping.

For development of *p-i-n* OLEDs, we recently proposed OLED having a 40-nm-thick alpha-sexithiophene (α-6T) hole transport layer doped with a strong electron acceptor of 2 mol%-2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F$_4$-TCNQ) and a 20-nm-thick phenyl-dipyrenylphosphine oxide (POPy$_2$) electron transport layer doped with a strong electron donor of 30 mol% Cs [1]. Our *p-i-n* OLED using the DCM:Alg$_3$ emitting layer sandwiched with the F$_4$-TCNQ:α-6T and Cs:POPy$_2$ transport layers exhibited an extremely low driving voltage of 2.9 V at 100 mA/cm^2, which is the lowest value ever reported (**FIG2**). Moreover, we observed bright EL from the DCM:Alg$_3$ layer at a low driving voltage: e.g., 1000cd/m^2 at only 2.4 V.

We further demonstrate that mixing of organic/organic heterojunction interfaces leads to a reduction in the driving voltage required for OLEDs (**FIG3**). We manufactured multilayer OLEDs with mixed heterojunction interfaces composed of α-6T and POPy$_2$ carrier-transporting layers [2]. In the interface mixed OLED, we observed a low driving voltage of 3.6 V at a current flow of 100 mA/cm^2 and improved power

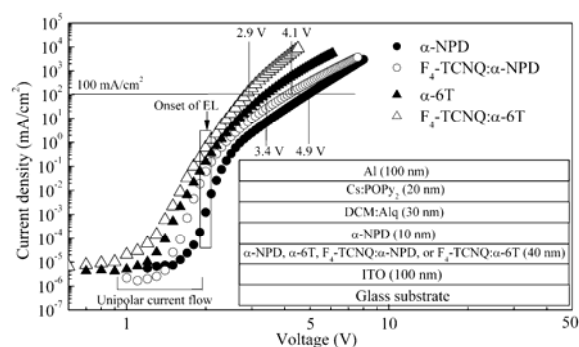**FIG1:** Organic Light Emitting Diode; HTL (hole transport layer), EML (emitter layer) and ETL (electron transport layer)

FIG2: J-V-L characteristics of p-i-n OLEDs. The OLED using the DCM:Alg$_3$ emitting layer sandwiched with the F$_4$-TCNQ:α-6T and Cs:POPy$_2$ transport layers exhibited the lowest driving voltage.
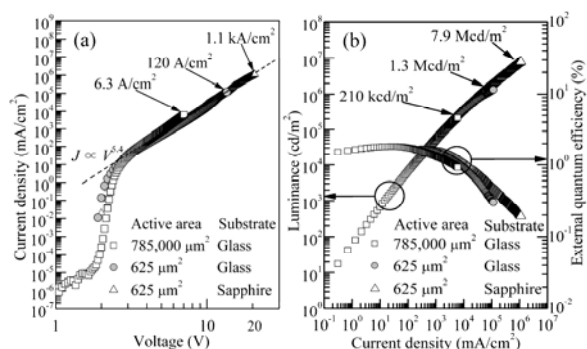
FIG3: J-V-L characteristics of p-i-n OLED having mixed organic interfaces. The OLED with small device size with a sapphire substrate resulted in the highest current over 1KA/cm^2.

conversion efficiency. We investigated how much current can flow through this OLED with the aim of fabricating electrically pumped organic laser diodes. We found that an OLED of this type with a small active area of 625 μm^2 on a high thermal conductivity sapphire substrate can sustain high current densities of 1.1 kA/cm^2 and emits bright electroluminescence of 7.9

II. ORGANIC LIGHT EMITTING TRANSISTOR

The demand for fusing OLEDs and OFETs to produce organic LE-OFETs (**FIG4**) has been increasing aimed at achieving simplified organic active matrix displays. LE-OFETs not only contribute to increased apertures in the pixels of light-emitting elements but also the inexpensive fabrication of active matrix displays due to the reduced number of switching thin-film transistors (TFTs). Further, controlling the carrier accumulation and successive carrier injection from both source and drain electrodes by applying a gate bias is a unique method of providing charge carriers in organic layers. Elucidation of the detailed mechanism has attracted a great deal of attention in this research field.

Recently, there have been several reports on LE-OFETs using tetracene, oligo-thiophene, fluorine-based polymers, carbon nanotubes, and phenylene-vinylene-based polymers. We also reported on OLEFETs using 2,4-bis(4-(2'-thiopheneyl)phenyl)thiophene (TPTPT) as an active layer, demonstrating a maximum external EL quantum efficiency of η_{ext}= 6.3 x 10^{-3} % with a short channel length (L$_{SD}$= 0.8 μm) between the source and drain (S-D) electrodes. Although these reports demonstrated appreciable electroluminescence (EL), η_{ext} is still very low, which is due to inefficient electron accumulation and injection from the drain electrode. To achieve efficient LE-OFETs, it has been necessary to prepare adequate organic materials with both electroluminescence and transistor characteristics. However, it is rather difficult to find candidates from well established OLED materials, since most OLED active materials have no high-performance FET characteristics probably due to their amorphous morphologies. The recent progress in OFETs has revealed that highly packed molecular thin films with tight inter-molecular π-stacking have demonstrated
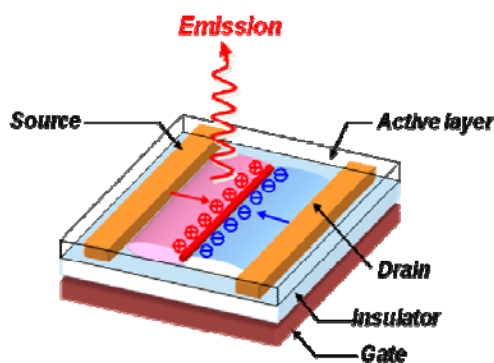

FIG4: Light Emitting FET.

pronouncedly high carrier mobilities exceeding ~1 cm^2/V·s. In particular, condensed aromatic compounds such as rubrene have demonstrated a high FET mobility of μ_{FET} ~10 cm^2/V·s in the form of a single crystal. Instead of having a high performance TFT function, however, most TFT active materials demonstrate rather weak PL due to their strong molecular packing, i.e., concentration quenching, meaning they are useless in light-emitting applications. Therefore, we need to satisfy the demand and find organic materials that provide both light-emitting and transistor characteristics. Since condensed aromatic polyacene derivatives generally demonstrate rather good FET characteristics and some acene derivatives, e. g., anthracene, have demonstrated high PL efficiency over ~50 % even in single crystal form, we explored various polyacene derivatives and discovered that a tetraphenylpyrene (TPPy) vacuum-deposited film has typical p-type FET characteristics with a high PL quantum efficiency of 68±3 % even in a neat vacuum deposited film [3]. To achieve higher PL efficiency, we doped rubrene into a TPPy host. We observed that doping various highly fluorescent molecules into a TPPy host resulted in significant improvements to PL efficiency, although some dopants completely eliminated TFT characteristics, and adding only specific dopants effectively maintained both TFT and PL characteristics. It is likely that no significant changes to TPPy aggregated morphology, i.e., molecular packing or grain size, by rubrene doping will contribute to retaining transistor characteristics.

We observed that the formation of a short channel length between the source and drain electrodes significantly increases carrier injection and EL efficiencies. We investigated the LE-OFET characteristics of a 1wt%-rubrene:TPPy co-deposited layer using various channel lengths (L$_{SD}$= 0.4 μm-10μm), and found that the LE-OFET characteristics were strongly dependent on the channel length. We also employed double-layered MgAu/Au and Al/Au S-D electrodes, aimed at achieving both efficient hole and electron injection. By optimizing active layer's materials and device parameters, we obtained various emission colors with rather high EL efficiency around 0.1~1% [4].

However, achieving high luminance efficiency in p-channel unipolar LE-OFETs was rather difficult because the number of the electron injected was significantly low compared to that of holes, and their

emission regions were always located at the vicinity of their drain contacts, leading to exciton quenching by metal absorption. On the other hand, the balance of holes and electrons is perfectly equal in ambipolar operation mode because accumulation layers of holes and electrons can co-exist in the channel. Recently, we prepared ambipolar OFETs based on a vacuum-deposited blue-emitting organic thin film. We used an organic semiconductor of 4,-4'-bis(styryl)biphenyl (BSBP) to prepare efficient LE-OFETs with high mobility [5]. Although the active layer in LE-OFETs is expected to have both high carrier mobility and high PL efficiency, balancing these two factors in a neat film is generally quite difficult. The strong π-π interactions of the planer molecules, such as tetacene, are preferable for intermolecular charge transport. On the other hand, using planar molecules usually leads to quite low PL efficiency in the neat films due to strong concentration quenching. Therefore, we carefully designed BSBP to balance carrier mobility and PL efficiency. We used a twisted bi-phenyl central unit to prevent strong π-π interactions for obtaining high PL efficiency, and relatively planar styrylbenzene end groups to contribute for efficient charge transport. Furthermore, we prepared ambipolar OFETs without breaking high vacuum during device preparation and measurement because electrical properties of organic semiconductors are quite sensitive to device preparation and measurement conditions.

We found that a BSBP film provides balanced high PL efficiency of 20 % and high field-effect hole mobility of 0.01 cm^2/Vs. We achieved fabrication and successive measurement of ambipolar OFETs based on BSBP under high-vacuum without breaking vacuum. The application of an Al contact and a PMMA insulating layer allowed ambipolar operation, and light emission was observed when both hole and electron accumulation layers co-existed in the channel region (**FIG5**). We found that simultaneous compatibility of low electron traps can be achieved by controlling the organic/metal and organic/insulator interfaces, device preparation, and measurement conditions under high vacuum.

To achieve ambipolar FETs, it is crucial to provide channel semiconductors that allow dual operation of *p*- and *n*-types. However, most metal-oxide semiconductors
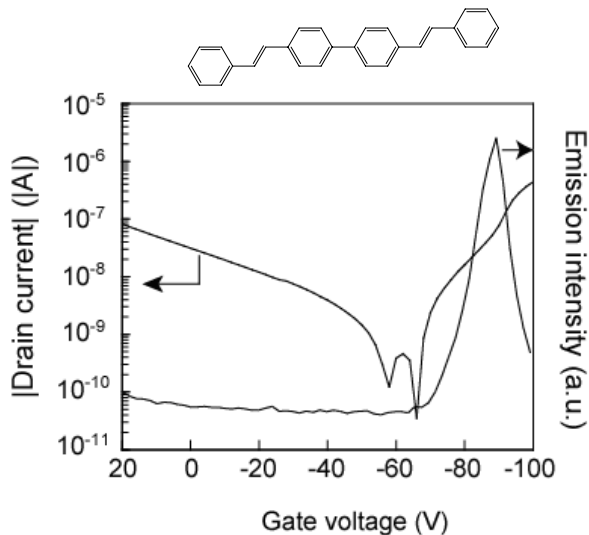
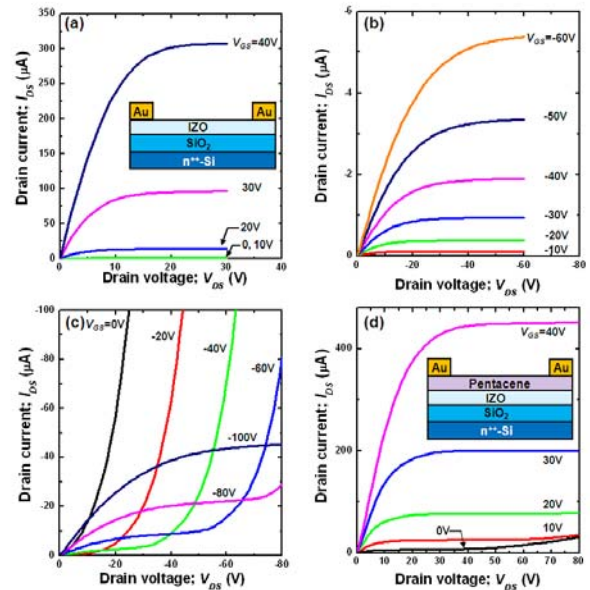**FIG5:** Ambipolar LE- FET characteristics using BSBP under drain voltage of V_d=-100V.

FIG6: Output characteristics of indium-zinc-oxide-FET (a), pentacene-FET (b) and FET based on indium-zinc-oxide/ pentacene heterostructure (c, d), respectively. (c) and (d) have *p*-type and *n*-type operation.

only have *n*-type characteristics, and very few devices with *p*-type operation have been identified. Organic semiconductors, on the other hand, demonstrate mostly *p*-type semiconducting behavior, and some organic materials, such as C60, copper hexadecafluoro phthalocyanine, fluorine substituted pentacene, perylene-3,4,9,10-tetracarboxylic dianhydride, and tetracarboxylic dianhydride, demonstrate *n*-type operations under strictly controlled environmental conditions. Furthermore, a high electron mobility that is stable in air is still problematic, even though some devices have shown excellent ambipolar operation. Thus, we decided to develop high-performance ambipolar FETs by combining *n*-type metal-oxide semiconductors and *p*-type organic semiconductors.

We recently demonstrate the fabrication of an ambipolar FET based on an organic-inorganic hybrid-structure that has as an active channel layer consisting of pentacene as the *p*-type layer and In_2O_3-5wt% ZnO as the *n*-type layer [6]. Although the FETs based on an indium-zinc-oxide or pentacene single layer only showed unipolar FET characteristics, the hybrid FET showed definite ambipolar FET characteristics (**FIG6**). We obtained a high saturated field-effect hole and electron mobilities of 0.14 and 13.8 cm^2/Vs. Furthermore, we demonstrated electro- luminescence from hybrid FETs using tetracene as an emitting layer.

III. ORGANIC LASER DIODE

Over recent years, a wide variety of challenges aiming for electrical pumping of organic laser diodes have been addressed. However, organic laser diodes (**FIG7**) have still not been realized owing to their high lasing threshold under electrical pumping. To reduce lasing threshold, a variety of organic semiconductors, including not only small molecular materials but also conjugated polymers, have been developed. Potential materials for low amplified-spontaneous-emission (ASE)
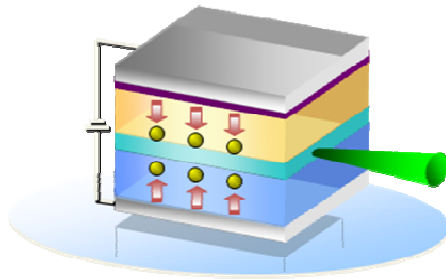
FIG7: Organic Laser Diode.

thresholds are spiro derivatives, which show high photo-luminescence (PL) quantum efficiency (Φ_{PL}) and low ASE thresholds in solid-state thin films. For example, 2,2',7,7'-tetrakis(9,9'-spirobifluoren-2-yl)-9,9'-spiro-bifluorene) (4-spiro^2) and 2',7'-Bis(biphenyl-4-yl)-2-(5-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-2-yl)- 9,9'-spirobifluorene (spiro-SPO) show low ASE thresholds of E_{th}=3.2 and 1 μJ/cm^2, respectively [7].

We recently demonstrated that bis-styrylbenzene derivatives (BSBs) have excellent PL and ASE characteristics in solid-state thin films under optical excitation. In particular, 4,4'-bis[(*N*-carbazole)styryl] biphenyl (BSB-Cz) showed a high Φ_{PL}=90±2%, short fluorescence lifetime of τ_{Flu}=of 1.0 ns, and a low ASE threshold of E_{th}=0.32 μJ/cm^2 when doped into a wide energy gap 4,4'-bis(9-carbazole)-2,2'-biphenyl (CBP) host at a concentration of 6 wt%. Further, we designed and synthesized novel spiro concept derivatives, namely, 2,7-bis(*N*-carbazolyl)-9,9'-spirobifluorene (spiro-Cz) and 2,7-bis[4-(*N*-carbazole)phenylvinyl]-9,9'-spiro-bifluorene (spiro-SBCz), and report on their PL, ASE and electroluminescence (EL) characteristics. In particular, we observed an extremely low ASE threshold of E_{th}=0.11±0.05 μJ/cm^2 (220 W/cm^2) in the spiro-SBCz-doped CBP film (**FIG8**). We also fabricated an organic light-emitting diode (OLED) and the light-emitting organic field-effect transistor (OFET) using the 9,9'-spirobifluorene derivatives. We confirmed that the spiro-SBCz thin film functions as an active light emitting layer in OLED and FET. The OLED showed a
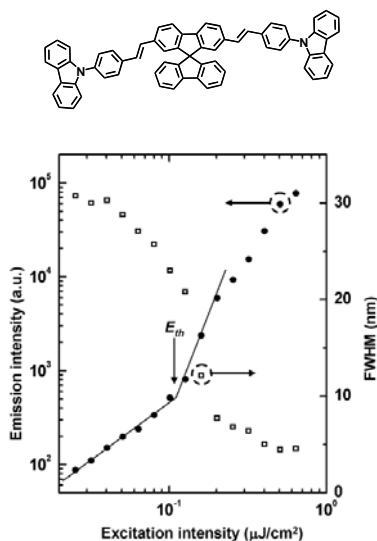
high external EL quantum efficiency of η_{ext}=3.2±0.2%. Further, the OFET showed significant linear EL under p-type operation which will lead to future organic laser diodes.

Finally we mention unusual spectral narrowing that have a TE mode with λ_{FWHM} = 3.4 nm in a 6-wt% -4,4'-bis-[(*N*-carbazole)styryl]-biphenyl(BSB-Cz):CBP film under CW excitation [8]. Although we observed no clear threshold characteristics on the spectral narrowing, the polarized and narrowed emission characteristics indicates occurrence of light amplification, which is induced by cut-off mode in optical waveguides. We mention outlook of the possibility of electrical pumping using this unusual light amplification [9].

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FIG8: ASE characteristics of spiro-SBC$_Z$:CBP film.