Highly Efficient Organic Light-Emitting Diodes Doped with Thiophene/Phenylene Co-Oligomer

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Research on organic light-emitting diodes (OLEDs) has been intensive due to their high potential for use in low-cost, lightweight, flexible display and lighting applications.[1,2] Doping fluorescent or phosphorescent organic guest molecules in a wide-energy-gap host layer, which is widely used in the manufacturing of high-performance OLEDs, is the key technique.[1–9] The introduction of this guest−host layer into OLEDs leads to the enhancement of electroluminescence (EL) efficiencies[3] and operational stability.[9] Multilayer OLEDs, having highly efficient phosphorescent iridium complexes doped in the appropriate host matrices, can reach an internal EL quantum efficiency of nearly 100%.[4,5,7] Thus, OLED performance is markedly dependent upon light-emitting and electronic characteristics of guest molecules.

We focused our attention on a thiophene/phenylene co-oligomer of 1,4-bis(5-phenyl-2-thienyl) benzene (AC5) as an emitting guest for OLEDs. The molecular structure of AC5 is shown in Figure 1. This material was originally synthesized by Hotta et al.[10] and has already been used as a *p*-type semiconductor layer in organic field-effect transistors (FET).[11,12] Previously reported hole mobilities of FETs comprising polycrystalline films and single crystals of AC5 ranged from 10^{-3} to 10^{-2} cm^2 V^{-1} s^{-1}. Moreover, this material possesses a high fluorescent quantum efficiency of 74% in a solution[13] and low amplified spontaneous emission threshold energies in crystals.[14,15] The variability of the total number of thiophenes and phenylenes provide different π-conjugation lengths and a wide spectral range of fluorescnce.[13] Suzuki et al. realized bright EL from OLEDs doped with phenyl-substituted oligothiophenes.[6] These excellent electrical and light-emitting characteristics of AC5 give it high potential as an emitting dopant for OLEDs. However, since EL characteristics of AC5 have never been reported, we selected AC5 as an dopant to investigate its EL characteristics.

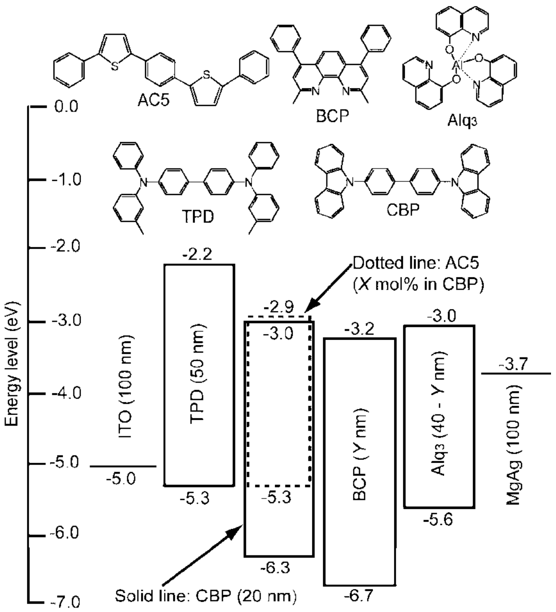

Figure 1. Chemical structures of AC5, TPD, CBP, BCP, and Alq$_3$ molecules and energy-level diagram of AC5-doped OLED.

Our OLED structure was composed of a glass substrate, an indium tin oxide (ITO) anode layer (100 nm), an electron-blocking hole-transport layer (50 nm) of *N*,*N*′-di(*m*-tolyl)-*N*,*N*′-diphenylbenzidine (TPD), an emitting layer (20 nm) of 4,4′-bis(carbazol-9-yl)-2,2′-biphenyl (CBP) doped with AC5 at *X* mol %, a hole-blocking electron-transport layer (*Y* nm) of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), an electron-transport layer (40−*Y* nm) of tris-(8-hydroxyquinoline) aluminum (Alq$_3$), and a MgAg cathode layer (100 nm). We varied the AC5 doping concentrations (*X*) ranging from 1 to 8 mol % and varied the BCP thickness (*Y*) ranging from 10 to 30 nm. The chemical structures of the molecules and the energy-level diagram of the OLED are also shown in Figure 1. This OLED structure is frequently used to confine excitons in the CBP layer,[16–19] and using the CBP host matrix can prevent concentration quenching

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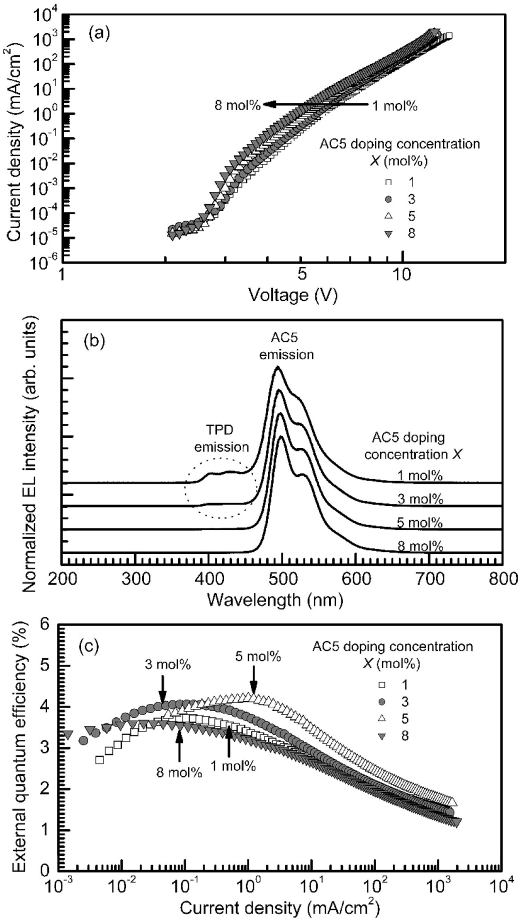

Figure 2. (a) $J-V$ characteristics, (b) EL spectra at 100 mA/cm^2, and (c) $J-\eta_{\mathrm{ext}}$ characteristics of AC5-doped OLEDs with various X's and constant Y of 10 nm.

of excited-state molecules.[3] In the present work, we report how the variation of X's and Y's affect the performance of the OLEDs in order to clarify their current flow and EL mechanisms. As the result of the optimizations of X's and Y's, we obtained a very high external quantum efficiency (η_{ext}) of 4.8% in the OLED with $X = 5$ mol % and $Y = 30$ nm. Experimental details are available in Supporting Information.

The current density–voltage (*J–V*) characteristics of the OLEDs with varying X (ranging from 1 to 8 mol %) and a constant Y of 10 nm are shown in Figure 2a. The driving voltages decreased as the X's increased from 1 to 8 mol %. The driving voltages at a current density of 100 mA/cm^2 were 9.7 ± 0.2 V for $X = 1$ mol %, 9.2 ± 0.1 V for $X = 3$ mol %, 8.8 ± 0.1 V for $X = 5$ mol %, and 8.6 ± 0.1 for $X = 8$ mol %. We previously demonstrated that $J-V$ characteristics of this type of the OLED structure are strongly influenced by a hole injection process from TPD to dopant molecules due to the largest hole injection barrier of 1.0 eV at the TPD/CBP interface.[19] Since the highest occupied molecular orbital energy levels of TPD and AC5 (−5.3 eV) are well aligned (Figure 1), holes are more preferably injected from TPD to AC5 than from TPD to CBP. Therefore, we attribute the voltage decrease to the enhancement of hole injection from TPD to AC5 instead of CBP. Since the holes injected into AC5 are less likely to transfer through the doped CBP layer via hopping between neighbor AC5 molecules due to the large hopping distance, we infer that the injected holes are confined in the AC5 molecules and are recombined with electrons near the TPD/CBP interface.

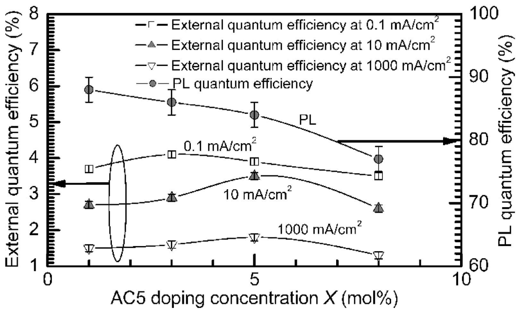

Figure 3. External quantum efficiencies at 0.1, 10, and 1000 mA/cm^2 vs AC5 doping concentrations of AC5-doped OLEDs and PL quantum efficiencies vs AC5 doping concentrations of AC5-doped CBP films.

The EL spectra of the OLEDs with various X's and a constant Y of 10 nm at a current density of 100 mA/cm^2 are shown in Figure 1b (the EL spectra of the OLEDs operated at 1, 10, and 100 mA/cm^2 are available in Supporting Information). We observed a large EL peak originating from electrically excited AC5 molecules at ≈500 nm in each spectrum. However, there was a small EL peak originating from electrically excited TPD molecules at a shorter wavelength in the EL spectra of the OLEDs with $X = 1$ and 3 mol %. The AC5 doping levels higher than 5 mol % were required to obtain pure EL from AC5 under electrical excitation. The EL mechanisms of the OLEDs involve CBP-to-AC5 Förster energy transfer and direct carrier recombination on AC5 molecules. Since most holes are directly injected and confined in AC5 molecules, the latter mechanism is more dominant than the former.

We obtained a very high η_{ext} of 4.2% in the OLED doped at $X = 5$ mol %. The $J-\eta_{\mathrm{ext}}$ characteristics of the OLEDs are shown in Figure 2c. The maximum η_{ext} was 3.7 ± 0.1% for $X = 1$ mol %, 4.1 ± 0.1% for $X = 3$ mol %, 4.2 ± 0.1% for $X = 5$ mol %, and 3.6 ± 0.1% for $X = 8$ mol %. The η_{ext} at 0.1, 10, and 1000 mA/cm^2 are plotted as a function of X in Figure 3. The X, which provided the highest η_{ext}, was 3 mol % at 0.1 mA/cm^2 and 5 mol % at 10 and 1000 mA/cm^2. We are aiming at realizing electrically pumped organic laser diodes (OLDs) as a post-OLED application. For this aim, an increase in η_{ext} at high current densities is required to induce electrical amplification. From the results shown in Figures 2b,c and 3, we concluded the best X to be 5 mol % for fabricating OLDs.

The η_{ext} can be expressed as the equation,[20] $\eta_{\mathrm{ext}} = \eta_{\mathrm{out}}\eta_{\mathrm{e/h}}\eta_{\mathrm{exciton}}\eta_{\mathrm{PL}}$, where η_{out} is the light out-coupling efficiency, $\eta_{\mathrm{e/h}}$ is the charge balance factor, η_{exciton} is the efficiency of the singlet or triplet exciton generation, and η_{PL} is the photoluminescence (PL) quantum efficiency of the emitting layer. To investigate the relationship between η_{ext} and η_{PL}, we prepared CBP films (100 nm) doped with AC5 at various X mol % on quartz substrates and measured their η_{PL} using an integrating sphere system (C9920-02, Hamamatsu Photonics Co., Ltd.). The η_{PL} was 88 ± 2% for $X = 1$ mol %,

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86 ± 2% for $X = 3$ mol %, 84 ± 2% for $X = 5$ mol %, and 77 ± 2% for $X = 8$ mol %, which are also plotted as a function of X in Figure 3. The η_{PL} monotonically increased by decreasing the X's from 8 to 1 mol % due to the suppression of concentration quenching. However, we have not found a clear relationship between η_{ext} and η_{PL}. We attribute the decrease in η_{ext} at a lower X to insufficient carrier recombination on AC5 molecules, which resulted in the observation of the undesirable TPD emission shown in Figure 2b. On the other hand, the decrease in η_{ext} at a higher X is probably due to the decrease in η_{PL}. Besides the η_{PL}, the charge balance factor of $\eta_{e/h}$ affects the η_{ext}, as the equation above indicates. In our OLEDs, the $\eta_{e/h}$ must be changed depending upon the X's due to the change of a hole injection efficiency at the TPD/CBP interface and a carrier mobility in the AC5-doped CBP layer. Therefore, we speculate that the maximum η_{ext} at a certain J were dependent on X's, as shown in Figure 3.

Since the zero field hole mobility of TPD (7.0×10^{-4} cm^2 V^{-1} s^{-1})[21] is much higher than the zero field electron mobilities of BCP (2.3×10^{-8} cm^2 V^{-1} s^{-1})[22] and Alq_3 (2.9×10^{-9} cm^2 V^{-1} s^{-1}),[23] the number of holes is expected to be higher than the electrons in the carrier recombination zone, probably lowering $\eta_{e/h}$ and η_{ext}. To balance the number of electrons and holes in the carrier recombination zone, we varied the BCP thickness (Y) ranging from 10 to 30 nm.

Figure 4a,b shows the $J-V$ and $J-\eta_{ext}$ characteristics of the OLED with the optimized X of 5 mol % and various Y's. The driving voltages decreased, and the η_{ext} increased as the Y's were increased from 10 to 30 nm. The driving voltage at a current density of 100 mA/cm^2 and the maximum η_{ext} were 8.8 ± 0.1 V and 4.2 ± 0.1% for $Y = 10$ nm, 8.0 ± 0.1 V and 4.5 ± 0.1% for $Y = 20$ nm, and 7.3 ± 0.2 V and 4.8 ± 0.1% for $Y = 30$ nm. This voltage decrease is attributable to the enhancement of an electron current because the BCP layer has a higher electron mobility than the Alq_3 layer, as mentioned above. The OLED with $X = 5$ mol % and $Y = 30$ nm had the highest η_{ext} of 4.8% among the devices. The η_{ext} of the OLEDs with the thicker BCP layer was improved at low current densities due to the enhanced electron current and improved $\eta_{e/h}$. Since a larger density of excitons is generated in OLEDs with higher η_{ext}, the η_{ext} of the OLEDs with the thicker BCP layer markedly decreased at high current densities, which may have been caused by singlet−singlet and singlet−polaron exciton annihilation.[24,25]

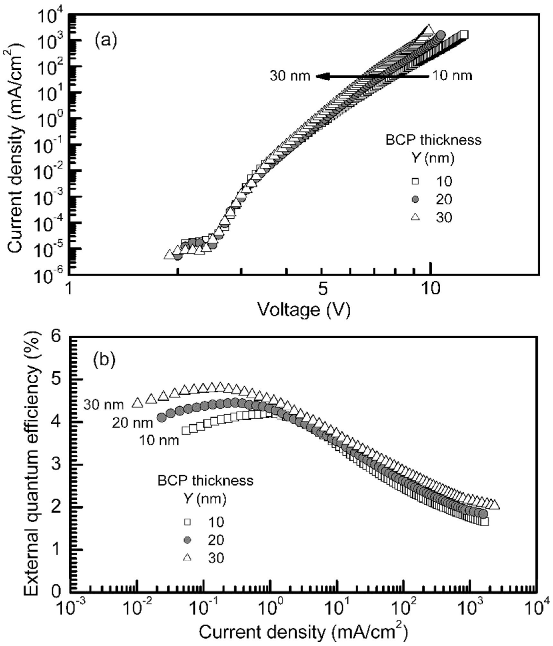

Figure 4. (a) $J-V$ and (b) $J-\eta_{ext}$ characteristics of AC5-doped OLEDs with optimized X of 5 mol % and various Y's.

Therefore, the BCP thickness appeared to exhibit stronger effect on η_{ext} at low current densities than at high current densities. We recently demonstrated that aligning energy levels of neighboring organic layers and emitting molecules prevents a decrease in η_{ext} at high current densities,[26] which will solve this annihilation problem.

In conclusion, we demonstrated that a thiophene/phenylene co-oligomer of AC5 doped in a wide energy-gap CBP host matrix layer is an excellent fluorescent dopant for manufacturing high-efficiency OLEDs. Controlling the doping level of AC5 and balancing the number of electrons and holes injected into the doped CBP layer were found to be crucial to obtain a high η_{ext}. By optimizing these conditions, we obtained a very high η_{ext} of 4.8%. This value is the highest ever reported in OLEDs doped with a thiophene/phenylene co-oligomer emitter. We emphasize that a thiophene/phenylene co-oligomer with excellent light-emitting and electrical characteristics is useful for developing next-generation organic electronic devices such as electrically pumped OLDs and organic light-emitting transistors.

Supporting Information Available: Experimental details and EL spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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