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Universal electron transporting layers via mixing two homostructure molecules with different polarities for organic light-emitting diodes

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ABSTRACT

In general, electron transport layer (ETL) in organic light-emtting diodes (OLEDs) consists of single component of electron transporting material (ETM) or a mixture with n-dopant such as 8-hydroxyquinolinolato-lithium (Liq). However, there exists a limit to controlling a wide range of carrier density in OLEDs according to the required characteristics of the devices due to electrically insulating property of Liq. Here, we suggest a universal strategy to construct an efficient ETL. We synthesized two ETMs, diphenyl-[4-(10-phenyl-anthracene-9-yl)-phenyl]-amine (An-Ph) and phneyl-[4-(10-phenyl-anthracene-9-yl)-phenyl]-pyridin-3-yl-amine (An-Py) that have the same core structures with different polarities in functional groups. The electrical characteristics of electron-only-devices (EODs) were investigated by space charge limited current (SCLC) modeling and impedance spectroscopy analysis. Interestingly, the homostructure type ETL composed of An-Ph and An-Py showed not only superior electron transporting capability, but also the possibility of controlling electron injection and transporting in a wide range compared to the heterostructure type ETL of An-Ph and Liq. Compared to the An-Ph-only EOD, the electron mobility in 75% An-Py-mixed homostructure EOD increased by almost 4 orders of magnitude. Such dramatic variation of electron mobility was achieved thanks to the molecular design strategy to separate charge injection and charge transport regions within a molecule, which consequently induced the giant surface potential (GSP) effect between the ETL/cathode interface. As a result, the external quantum efficiency (EQE) of blue fluorescent and phosphorescent OLEDs with the homostructure ETLs was enhanced by 28.6% and 34%, respectively, compared to that of each control device without manipulating outcoupling effects.

1. Introduction

Organic light-emitting diodes (OLEDs) consist of an emission layer, charge injection, and transport layers between two electrodes. Both efficiency and lifetime of OLED devices strongly depend on the balance of electron and hole which are injected from the electrodes and transported into the emission layer (EML). Therefore it is very important to control the balance of charge injection for a variety of chromophores and host materials for EMLs. In order to maximize the device performances out of red, green, and blue EMLs simultaneously, not only various EML materials are investigated, but also charge transporting materials are developed. Thus, the research on OLEDs has been mainly conducted to improve and optimize the charge balance in the EML by developing new charge transporting materials [1–3]. However, it takes a lot of time and cost to develop new charge transport materials according to device architectures, EML materials, and the required device characteristics. As widely known, the same hole transporting layer (HTL) has been used since the OLED panels were commercially available for cellphones. However, the electron transporting layer (ETL) has been continuously and newly developed for every generation of cellphones with newly-developed EMLs. In general, ETL is composed of an electron transporting material (ETM) and an additive material in commercial OLED products. Thus, for the evolution of OLED technologies, both new ETMs and the optimized mixing ratio of the additive material should be continuously developed. As additive materials in ETLs, n-dopant materials such as alkali metals or air-stable precursor molecules [4–8]. In the

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OLED industry, 8-hydroxyquinolinolato-lithium (Liq) has been widely used in the ETL for elongated device lifetime. However several issues still remain with Liq. First, the charge transporting characteristics strongly depend on the co-deposited ETMs. Second, there is a limit to control electrical mobility and current density in a high electric field depending on the content of Liq due to the electrically insulating nature and variation of intermolecular packing property [9,10]. Finally, Liq is known to form a trimer or tetramer structure under thermal stress, affecting an undesirable effect on the charge balance in EML due to its small size [11,12].

Here, we propose a universal methodology to construct an Liq-free ETL that can adjust the current density of OLEDs in a wide range by mixing two ETMs with the same core and different polarities due to functional groups. The molecular design strategy was to separate charge injection and charge transport regions within a molecule. Diphenyl-[4-(10-phenyl-anthracene-9-yl)-phenyl]-amine (An-Ph) and phneyl-[4-(10-phenyl-anthracene-9-yl)-phenyl]-pyridin-3-yl-amine (An-Py) were designed and synthesized. The fused aromatic anthracene was chosen as core units where electrons are delocalized and the overlap of intermolecular wavefunctions easily occurs. On the other hand, functional groups have similar structures, but different polarities induced by phenyl and heteroaromatic rings. Since the size of the entire molecules are almost identical and the molecular weights are similar, the deposition temperature and thermal stability would not be significantly different.

When permanent dipole moment (PDM) induced by the asymmetric molecular structure is present in a deposited film, spontaneous orientation polarization (SOP) can be formed in a particular direction, which induces counter charges on the heterointerface of the organic layer under the electric field. The magnitude of the SOP results in a thickness-dependent internal potential gradient, called giant surface potential (GSP) effect, which was reported to improve the charge injection performance in organic photovoltaic devices [13–15]. According to Ref. [16] the dipole moment of EML can be adjusted by mixing polar and non-polar materials at different ratios [16], thus a polar An-Py and a non-polar An-Ph were mixed in a wide range (0–75 wt%) to construct an efficient ETL.

In addition, we divided fabricated devices into two groups, homostructure (An-Ph mixed with An-Py) and heterostructure (An-Ph mixed with Liq) type and investigated their electrical characteristics with respect to the mixing ratio through space charge-limited current (SCLC) theory and impedance spectroscopy. Finally, up to 33.7% and 34.4% of efficiency enhancement with homostructure ETLs were confirmed in blue fluorescent and phosphorescent OLEDs, respectively.

2. Results and discussion

2.1. Material design and calculation of electronic properties

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were carried out for ground state molecules. The geometries in the gas phase were optimized by the DFT method using the B3LYP exchange-correlation function with the 6-31G* basis set in the Gaussian 09 program package [17]. Fig. 1(a) and Figure S1 show the electronic populations of the lowest unoccupied molecular orbital (LUMO) state and the highest occupied molecular orbital (HOMO) state of An-Ph and An-Py, respectively. Regarding the HOMO states, the electron density of An-Ph was localized on triphenyl amine, while those of An-Py on anthracene. However, the electron density of the LUMO states in both molecules was localized on the same anthracene core. Thus, it is expected that an electron pathway can be easily formed due to the overlap of wavefunctions between two molecules when An-Py and An-Ph are mixed. It has been reported that the interaction between nitrogen in heteroaromatic rings of molecule and cathode metal, called coordination reaction reduces the electron injection barrier at ETL/metal surface [18–20]. Fig. 1(b) illustrates an electron injection process from metal



Fig. 1. (a) The calculated LUMO of An-Ph and An-Py (b) Illustration of electron injection from Al atoms in cathode to non-bonding sp^2 orbital in pyridine. Cloud shape represents the coordination reaction between Al and nitrogen.

atom in cathode to non-bonding sp^2 orbital in pyridine of An-Py. Furthermore, molecular dipole moment, μ (D) of An-Py and An-Ph was calculated to be 2.317 D and 0.2809 D, respectively. Thus, it is expected that the degree of PDM will be increased when An-Py is mixed with An-Ph.

2.2. Synthesis and photophysical and electrochemical analysis

As shown in Scheme 1, An-Ph and An-Py were synthesized by twostep and one-step procedure, respectively. At first, 9-(4-bromophenyl)-10-phenylanthracene was prepared through Suzuki coupling reaction with (10-phenyl-9-anthryl)boronic acid and 1-chloro-4-iodo-benzene. After then, Buchwald-Hartwig reaction was carried out with diphenylamine to obtain An-Ph. Pre-purchased 9-(4-chlorophenyl)-10-phenylanthracene and N-phenyl-3-pyridinamine were used to execute the same amination reaction to acquire An-Py. The final products were purified by recrystallization and vacuum sublimation to remove undesirable impurities. To confirm the chemical structure of final products, ¹H and ¹³C nuclear magnetic resonance and mass spectroscopy were carried out (See Figure S2 \sim S4).

2.3. Physical properties

Fig. 2 shows UV-vis absorption and photoluminescence spectra of An-Ph and An-Py in dilute solution. The vibrational bands at 357-397 nm wavelength originated from 0 to 4 to 0-1 transition of anthracene moiety were measured in both An-Ph and An-Py [21]. The emission energies of An-Py and An-Ph were estimated to be 2.65 and 2.54 eV from peak wavelength, respectively. The electrochemical properties of An-Ph and An-Py were measured by cyclic voltammetry (CV). $E_{\mbox{\scriptsize LUMO}}$ was obtained from the onset of reduction potential (See Figure S5). E_{LUMO} was obtained from the formalism of $E_{LUMO} = E_{HOMO} + E_g$, where E_g is the onset energy of the absorption spectra. Therefore, the HOMO/LUMO levels of An-Ph and An-Py were estimated to be -5.34/-2.41 and -5.46/-2.40 eV, respectively. The HOMO and LUMO levels of An-Py were slightly lower than those of An-Ph due to electron-withdrawing pyridine. The thermal properties of the molecules were measured and their results are shown in Figure S6 and S7. The thermal decomposition temperature (T_d) of An-Ph and An-Pv was found to be 367 and 329 °C. respectively. The glass transition temperature (T_{q}) of An-Ph and An-Py was 101.7 and 100.2 °C, respectively. The high T_d ensures a good surface morphology and high thermal stability for vacuum deposition in OLED fabrication.

2.4. Analysis of electron-only devices

The electron transporting characteristics of An-Ph and An-Py were confirmed with electron-only devices (EODs). An-Py or Liq was mixed with An-Ph in the EODs. The detailed device structure of the EODs is



Scheme 1. Synthetic procedures of An-Ph and An-Py.



Fig. 2. UV absorption (dot) and PL spectra (solid line) of An-Ph and An-Py in DCM at room temperature.

described in the experimental section. Fig. 3(a) and (b) show the current density (J)-voltage (V) curves of the An-Ph-based EODs as a function of An-Py or Liq mixing ratio. Among the homostructure EODs, the device without An-Py mixed showed the lowest current density. However, as the mixing ratio of An-Py increased, the current density drastically increased. Figure S8 shows the J-V characteristics of An-Py-only and An-Ph-only EODs with and without EIL. The difference in electron injection and transport properties is distinct in the EODs without EILs. The electrons from Al cathode can be injected even without the help of EIL. Recently, coordination reaction between nitrogen-containing heterocycles with diffused Al atoms from cathode can reduce the electron injection barrier and facilitate the electron injection from cathode [20]. Even with Liq inserted as an EIL, An-Py showed much superior electron injection and transport properties to An-Ph. According to Ref. [20], the role of Liq as EIL is to simply reduce the workfunction of cathode due to its low charge neutrality level. These results strongly indicate that enven though LUMO levels of An-Ph and An-Py are almost identical, the electron injection from cathode to An-Ph does not occur efficiently since no coordination reaction between An-Ph and Al cathode is present. The electrons from cathode are easily and efficiently transferred to non-bonding sp^2 orbital in pyridine of An-Py and transported through anthracene cores as illustrated in Fig. 1(b). In addition to the enhancement of current density as a function of the An-Py mixing ratio, the

current injection defined by the transition voltage from Ohmic to trap charge-limited (TCLC) region was also improved as shown in Figure S9 (a). The variation of the transition voltage as a function of An-Py mixing ratio can be attributed to the increased dipole moment in the ETL called giant surface potential (GSP) effect. The GSP caused by doping polar molecules generates a polarization of ETL. Consequently, the polarization of ETL induces counter-charge in the interface between the ETL and cathode, lowering the electron injection barrier [22]. The GSP effect is proportional to the size of the dipole moment in the organic layer and relies on layer thickness as well as on the doping concentration of the polar molecule [15]. To confirm the GSP effect in homostructure ETL, the capacitance measurements were carried out for the EODs at 1 kHz frequency as shown in Figure S9(b). When the thickness of the ETL increased from 40 nm to 60 nm, the geometrical capacitance decreased since the capacitance is reciprocal to thickness. However, the voltage for carrier injection (Vin) was reduced from 2.24 V to 2.12 V, which clearly proves the GSP is present in the homostructure ETL. The charge injection mechanism of An-Ph and An-Py is schematically displayed in Figure S10. Since the GSP induces an internal electric field, the slope of energy levels are different in An-Ph and An-Py ETLs. Therefore, the flat band voltage for electron injection in An-Py is lower than that of An-Ph. On the other hand, the current density of Liq-mixed EODs exhibited significantly different behavior from the An-Py-mixed EODs. Similar to 25% An-Py-mixed EOD, the current density of 25% Liq-mixed EOD increased. However, the concentration of Liq increased from 25% to 50%, the current density surprisingly decreased. Moreover, the 75% Liq-mixed EOD showed not only the significantly reduced current density, but also the unstable current injection and transport behavior. This unusual electrical behavior can be understood in terms of the poor electron transporting property of Liq [9,23].

For further analysis of charge transporting properties, SCLC model was applied. SCLC model is a versatile method to obtain field-dependent mobility of organic layer. The field-dependent mobility can be expressed as Eqn. (1) taking into account the Pool-Frenkel effect [24–26], where μ_0 is zero-field mobility, β is field activation of mobility and *E* is an electric field.

$$\mu = \mu_0 \exp\left(\beta\sqrt{E}\right) \tag{1}$$

A monopolar SCLC conforming to Eqn. (1) proposed by Murgatroyd can be approximated as follows [27].

$$J = \frac{9}{8} \varepsilon \varepsilon_0 \frac{E^2}{L} \mu_0 \exp\left(0.89\beta \sqrt{E}\right)$$
⁽²⁾



Fig. 3. The current density (*J*)- voltage (*V*) and space charge limited current–electric fields characteristics of (a) and (c) An-Py- and (b) and (d) Liq-mixed EODs. The black lines are numerical fitting curves to the space charge limited behavior by Eqn. (2).

The dielectric constant $\varepsilon \varepsilon_0$ of organic bulk layer was assumed to be 3, and we estimated μ_0 and β from Eqn. (2). The fitting results are shown as the black solid lines in Fig. 3(c) and (d) and the calculated values are summarized in Table 1. The zero field mobility, μ_0 corresponds to charge hopping distance and molecular packing proclivities, and the electric field activation β is related to the degree of energetic disorder of organic film [24,28]. Thus, the greater the degree of μ_0 and/or β in terms of both morphology and density of state (DOS) is, the higher the charge mobility is. In our experimental results, the degree of energetic disorder (β) was not much different in the EODs. However, the zero field mobility of the An-Py-mixed EODs was up to 50 times larger than that of the Liq-mixed EODs at 75% mixing ratio. Therefore, as clearly shown in Table 1, the large difference in current density and the electron mobility was caused by the large difference in the zero field mobility rather than the electric field activation. Figure S11 shows schematic diagrams of An-Py- and Liq-mixed films under the electric field. In the homostrucutre ETL, the electron transporting pathway is formed by the orbital overlap of anthracene cores in An-Ph and An-Py molecules, resulting in a long charge hopping distance as in Figure S11(a). On the contrary, even though the electrons are injected from Liq molecules in EIL directly to Liq or to An-Ph molecules in the ETL, the orbital overlap between An-Ph

Table 1 Summary of zero-field mobility, field activation of mobility, mobility at 1 MV/ cm for EQDs.

Mixing ratio	An-Ph: An-Py x %			An-Ph: Liq x %		
	μ ₀ (cm [2]/Vs)	β (cm/ V)	μ (cm [2]/Vs)	μ ₀ (cm [2]/Vs)	β (cm/ V)	μ (cm [2]/Vs)
0%	$\begin{array}{c} \textbf{4.23}\times\\ \textbf{10}^{-10}\end{array}$	0.141	$\begin{array}{c} 2.80 \times \\ 10^{-9} \end{array}$	$\begin{array}{c} 4.23\times\\ 10^{-10}\end{array}$	0.141	$\begin{array}{c} \textbf{2.80}\times\\ \textbf{10}^{-9} \end{array}$
25%	2.49×10^{-9}	0.185	$7.95 imes 10^{-7}$	1.21 imes 10 ⁻⁹	0.184	$\begin{array}{c} \textbf{7.04}\times\\ \textbf{10}^{-7}\end{array}$
50%	$\frac{1.18}{10^{-8}}\times$	0.188	$\begin{array}{c} \textbf{4.47}\times\\ \textbf{10}^{-6}\end{array}$	$\begin{array}{c} \textbf{8.17}\times\\ \textbf{10}^{-10}\end{array}$	0.171	$\begin{array}{c} 2.29 \times \\ 10^{-7} \end{array}$
75%	$\begin{array}{c} 2.62 \times \\ 10^{-8} \end{array}$	0.192	$\begin{array}{c} 1.18 \times \\ 10^{-5} \end{array}$	4.16×10^{-9}	0.168	$\begin{array}{c} 3.09 \times \\ 10^{-7} \end{array}$
100%	$\begin{array}{c} 3.29 \times \\ 10^{-8} \end{array}$	0.194	1.66×10^{-5}	-	-	-

molecules is significantly reduced as the mixing ratio of Liq increases as shown in Figure S11(b). Thus, the hopping distance with Liq mixed was significantly reduced.

In order to further analyze the charge injection and transporting properties in the ETLs, impedance spectroscopy (IS) measurements were carried out. The IS a widely-used non-destructive method to analyze charge dynamics of organic photovoltaic devices and OLEDs. An OLED can be represented with an equivalent circuit consisting of series and parallel resistances and capacitors as Eqn. (3) [29–32].

$$Z = Re(Z) + iIm(Z) = R_L + \frac{R}{1 + w^2 R^2 C^2} - i \frac{wR^2 C}{1 + w^2 R^2 C^2}$$
(3)

 R_L is the contact resistance, R is the resistance of organic layer, w is the angular frequency in the measurement, C is the capacitance. When voltage is applied, two types of current flow are present. One is the displacement current that flows through the capacitor C of the organic layer and the other is the conductive current through the resistance R[33]. Since the organic layers are sandwiched between anode and cathode, the dielectric capacitance is present in the OLEDs. However, very little displacement current flows in low voltage regime as a result of the space charge and low carrier mobility of the organic materials. As the voltage increases, the conductive current begins to flow through the resistance of the organic material at the maximum point of Re(Z) when the reactance and the resistance become the same as described in Eqn. (4).

$$\operatorname{Re}(Z)_{max} = \frac{1}{\omega C} = R_L + \frac{R}{2} \approx \frac{R}{2}$$
(4)

In other words, $\text{Re}(Z)_{\text{max}}$ is the point at which the main current flow is converted from displacement to conductive current, and the voltage of $\text{Re}(Z)_{\text{max}}$ can be regarded as carrier injection voltage (V_{in}) from electrode to organic layer. Fig. 4 shows Re(Z) of the EODs as a function of voltage measured under 1 kHz, 50 mV AC bias conditions. First, in the case of homostructure type EODs, V_{in} at 0, 25, 50, 75, and 100% of An-Py mixing ratio gradually decreased to be 3.27, 2.48, 2.36, 2.30, and 2.24 V, respectively (see Fig. 4(a) inset). Note that the magnitude of Re (Z)_{max} decreases, which is also consistent with the increase of the current density in SCLC region in Fig. 3(a). Therefore, it is shown that the charge



Fig. 4. The Re(Z) – Voltage characteristics of EODs.

injection barrier and the electrical conductivity can be controlled according to the magnitude of the dipole moment of the ETL through mixing homostructure molecules with different polarities. In the case of the heterostructure EODs, as the mixing ratio of Liq increased from 25 to 50%, V_{in} surprisingly decreased while $\text{Re}(Z)_{max}$ increased. However, neither V_{in} nor $\text{Re}(Z)_{max}$ was not clearly defined in the 75% Liq-mixed EOD even though the role of Liq is to help charge injection for the existence of free Li with low workfunction between the cathode and ETL [23]. This result strongly suggests that it is extremely difficult to control the charge injection and the transport property at the same time by mixing Liq in a wide range.

2.5. Performances of OLEDs

Since the hole mobility is generally much higher than the electron mobility [34], the bottleneck of perfect charge balance and high efficiency is to supply electrons into EML. To test the capability of the electron injection and transporting by the homostructure ETL, we



Fig. 5. The device performances of FOLEDs (left) and PhOLEDs (right). (a) and (b) current density-voltage, (c) and (d) luminance-voltage, and (e) and (f) external quantum efficiency versus luminance.

fabricated a series of fluorescent OLEDs (FOLEDs) and phosphorescent OLEDs (PhOLEDs). In addition, 50 wt% Liq-mixed heterostructure ETL was also applied for comparison. The device structures are described in **Experimental section** and energy level diagram of FOLEDs and PhO-LEDs are represented in Figure S12.

The current density (J)-voltage (V)-luminance (L) of FOLEDs and PhOLEDs are shown in Fig. 5(a)~(f). The turn-on voltages of 0% An-Pymixed FOLED and PhOLED were 4.36 V and 4.20 V at 1 cd/m², respectively due to the inefficient electron injection by non-polar An-Ph. However, once An-Py was mixed with An-Ph, the turn-on voltage was significantly reduced down to 3.49 V and 3.88 V for 25% An-Py-mixed FOLED and PhOLED, respectively. Such dramatic decreases can be attributed to the efficient electron injection process from EIL to nonbonding sp^2 orbital in pyridine of An-Py and the GSP effect. Interestingly, the turn-on voltages were not decreased significantly in the 50 and 75% An-Py-mixed devices. This result implies that the number of nonbonding sp^2 orbital sites and the intensity of the GSP were almost saturated even in 25% An-Py-mixed ETL. However, compared to the turn-on voltages, the driving voltages at 10 mA/cm² of current density gradually decreased as the An-Py mixing ratio increased, indicating that the electron transporting property was sensitively affected by An-Py mixing ratos. In 50% Liq-mixed FOLED and PhOLED, 10.82 V and 9.75 V of the driving voltages at 10 mA/cm² were obtained, respectively due to the electrically insulating property of Liq. The electrical transporting properties of the FOLEDs and the PhOLEDs well corresponded to the results of the EOD experiments.

As well known, the EQE of OLED consists of the following factors, which are charge balance (γ), radiative exciton ratio ($\eta_{S/T}$), photoluminescence quantum yield (Φ_{PL}), and outcoupling efficiency (η_{OUT}) as shown in Eqn. (5).

$$EQE = \gamma \times \eta_{S/T} \times \varphi_{PL} \times \eta_{OUT}$$
(5)

As the mixing ratio increased, the \mbox{EQE}_{max} also increased in the FOLEDs. With an assumption of $\eta_{S/T} \Phi_{PL}$, and η_{OUT} to be 0.25, 0.79 [35], and 0.2, respectively, the charge balances of 0, 25, 50, and 75% An-Py-mixed FOLEDs were 0.71, 0.83, 0.91, and 0.95, In our FOLEDs, the increase of electron transporting into EML proportionally increase the charge balance and the device efficiency. On the other hand, the EQE_{max} of the PhOLEDs shows a different feature from that of the FOLEDs. The largest EQE_{max} was obtained from the PhOLED with 25% An-Py-mixed ETL. mCP is a widely-used host with hole transporting characteristics, which implies the host in the PhOLEDs is generally in an electron-deficient state. Thus, as the electron transporting increased by varying the mixing ratio of An-Py, the efficiency of the PhOLED was expected to increase accordingly. However, as the An-Py mixing ratio increased over 25%, the long-living triplet excitons were densely populated in the EML, leading to undesirable triplet-triplet annihilation and/or triplet-polaron quenching processes. In both the FOLED and the PhOLED with 50% Liq-mixed ETL, the EQE_{max} increased from 2.82% to 9.72%-3.47% and 10.03%, respectively as in An-Py-mixed devices. However, the roll-off characteristics of the Liq-mixd devices were distinctively different those of the An-Py-mixed devices. As the device performances were summarized in Table S1, when An-Py was mixed in the ETL, the EQEs at 10 mA/cm² maintained over 90% and 70% of the EQE_{max} of the FOLEDs and the PhOLEDs, respectively. The new concept of ETL by utilizing homostructure molecules with different polarities in this work clearly demonstrated a strategy to construct a universal ETL which operates in a wide range of current density and simultaneously exhibits superb roll-off characteristics and efficiency in fluorescent and phosphorescent devices.

The charge balance effect by homostructure ETL in PhOLEDs also can be noticed through current efficiency (See Table S1). There is significant increase from 19.25 cd/A in 0% device to 25.11 cd/A in 25% device and the current efficiency starts to decrease in highly doped devices. It is due to charge unbalance resulting from excessive injection of electrons into EML. At last, The FOLED and PhOLED with 50 wt% Liq doped ETL showed higher EQE_{max} (3.47%, 10.03%) than 0% device (2.82%, 9.72%), but the EQE roll-off were significantly severe than the other devices. Hence, we confirmed that the homostructure ETL with An-Ph and An-Py can be used universally for OLED, while Liq can not have wide range of mixing ratio in ETL affecting device performance. The electroluminescent spectra of FOLEDs and PhOLEDs are shown in Figure S13.

3. Conclusion

In this study, we proposed a univseral method to construct ETL called homostructure type that mixes two ETMs with the same core but with different polarity substituents. The electrical characteristics of the newly designed ETL were investigated through SCLC modeling and impedance measurements. As a consequence, the electron injection and transport capabilities were continuously improved depending on the mixing ratio in homostructure ETL, which has superior electron transport characteristics to the ETL with Liq. The mobility of homostructure type EOD doped 50% is 4.47×10^{-6} cm/V in 1 MV/cm electric field, which is 20 times higher than that of heterostructure type EOD with Lig at the same condition. The GSP effect and continuously decreasing the electron injection voltage of homostructure type ETL were confirmed by impedance measurement, which shows the possibility of controlling the electron density of the newly proposed ETL. These results are directly related to the performances of blue fluorescent and phosphorescent OLED following improvement of their device efficiency up to 33.7% and 34.4% respectively, as well as the driving characteristics. Consequently, the ETL with two homostructure materials that can easily manipulate electron transport characteristics is expected to be an effective alternative to conventional ETLs with Liq in display manufacturing.

4. Experimental section

4.1. Physical measurements

To obtain HOMO and LUMO of An-Ph and An-Py, cyclic voltammetry (CV) was conducted in nitrogen-purged dichloromethane with tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) as the supporting electrolyte at room temperature by electrochemical analyzer (PGSTAT101, E-Chem Technology). We used ferrocenium-ferrocene (Fc+/Fc) as standard material to calculate HOMO/LUMO of organic materials. The UV–vis absorption results and PL spectra were measured with dichloromethane as solvent (10^{-5} M) using a UV–Visible spectroscopy (Agilent 8453) and fluorescence spectrometer (LS55, PerkinElmer precisely). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was carried out under 100 °C/min condition in nitrogen atmosphere by Seiko Exstar 6000 instrument.

4.2. OLED fabrication

Indium tin oxide (ITO) coated glass with sheet resistance of 30 Ω /sq and thickness of 150 nm were cleaned in ultrasonic baths (acetone, methyl alcohol, distilled water, and ethyl alcohol) for 15 min each. Before depositing organic layers, pre-cleaned ITO-coated glass substrates were dried in a convection oven at 120 °C for 10 min. After then, the ITO/glass substrates were treated with O₂ plasma at 2×10^{-2} Torr and 125 W condition for 2 min. Organic layers were deposited by thermal evaporator with shadow mask under high vacuum (5 $\times 10^{-7}$ Torr) condition. Aluminum (Al) cathode was deposited at a rate of 10 Å/s. The deposition process, glass cap and UV-epoxy resin were used to prevent degradation from ambient condition. The getter was attached under the glass cap to absorb the residue moisture in the encapsulated device, which has an active layer of 3 \times 3 mm².

The EODs were fabricated as the following structure: ITO/TmPyPB

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(5 nm)/An-Ph:An-Py (or Lig) x wt.% (40 nm)/Lig (2 nm)/Al (100 nm), where x = 0, 25, 50, 75, 100 for homostructure EOD and 0, 25, 50 for heterostructure EOD.

The detailed device stack of emitting devices are ITO (150 nm)/2-TNATA (30 nm)/NPB (10 nm)/MADN:Pyrene-CN 2 wt% (20 nm)/ TmPyPB (5 nm)/ETL (40 nm)/Liq (2 nm)/Al (100 nm) for FOLEDs and ITO (150 nm)/2-TNATA (40 nm)/NPB (10 nm)/mCP (10 nm)/mCP: FIrpic 8 wt% (20 nm)/TmPyPB (5 nm)/ETL (40 nm)/Lig (2 nm)/Al (100 nm) for PhOLEDs, where ETL is composed of An-Ph:An-Py(or Liq) x wt. %, where x = 0, 25, 50, 75 for homostructure ETL and 50 for heterostructure ETL. In the device structure, 2-TNATA is 4,4',4"-Tris [2naphthyl (phenyl)amino]triphenylamine, NPB is N,N'-Di (1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine, TmPyPB is 1,3,5-Tri (mpyridin-3-ylphenyl)benzene. 2-Methyl-9,10-bis(naphthalen-2-yl) anthracene (MADN) and 1.3-Bis(N-carbazolvl)benzene (mCP) were used as host. (1,6-Bis(N-phenyl–CN–phenylamino)-pyrenes (Pyrene-CN) and Bis [2-(4,6-difluorophenyl)pyridinato-C2, N]iridium (III) (FIrpic) were used for sky blue fluorescent and phosphorescent dopant respectively.

4.3. OLED characterizations

The J-V-L characteristics and EL performance were measured using a source meter (model 2400, Keithley) and Chroma meter (CS-1000A) instrument. Impedance analyzer (Alpha-AN, Novocontrol) were used to obtain Re(Z). All measurements were conducted at room temperature.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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