This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
**Graphical Abstract**

Water-soluble 1,2,4-Triazole with Diethylene Glycol Monoethyl Ether Groups: Synthesis, Characterization and Application as Electron Injection Layer for PLEDs

Chia-Shing Wu, Yu-Sing Wu and Yun Chen*

*Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan

*Corresponding author: yunchen@mail.ncku.edu.tw

Novel electron injection material **3OTAZ** composed of aromatic 1,2,4-triazolyl core with three diethylene glycol ether groups enhances electroluminescence of HY-PPV.
Water-soluble 1,2,4-Triazole with Diethylene Glycol Monoethyl Ether Groups: Synthesis, Characterization and Application as Electron Injection Layer for PLEDs

Chia-Shing Wu, Yu-Sing Wu and Yun Chen*

Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan

*Corresponding author: yunchen@mail.ncku.edu.tw

Abstract

We design a novel electron injection material 3OTAZ composed of aromatic 1,2,4-triazolyl core with three diethylene glycol ether groups to enhance electroluminescence of PLEDs using environmentally stable aluminum cathode. Multilayer PLEDs [ITO/PEDOT:PSS/HYIPPV/EIL(3OTAZ)/Al] using 3OTAZ as electron injection layer (EIL) exhibit significantly enhanced device performance. The maximum luminous power efficiency and maximum luminance of the device with 3OTAZ as EIL were enhanced to 0.34 lm/W and 2970 cd/m$^2$, respectively, compared with those without EIL (0.006 lm/W, 230 cd/m$^2$). The turn-on voltage was also significantly reduced from 8.2 V to 4.3 V simultaneously. The performance enhancement has been attributed to improved electron injection which has been confirmed by the raise in open-circuit voltage ($V_{oc}$) obtained from photovoltaic measurements. Moreover, more balanced charges injection and transport has been achieved by inserting 3OTAZ which adjust hole-blocking effect investigated by hole-only devices. The results indicate that 3OTAZ is an excellent electron injection candidate in performance enhancement for PLEDs with high work function Al cathode.
**Introduction**

For more than two decades, polymer light-emitting diodes (PLEDs)\(^1\)\(^-\)\(^3\) have attracted continuous attention because of their low cost, easy processability, and the possibility of easily fabricating flexible, large-area displays. PLEDs are carrier injection devices, which basically require balanced hole and electron injection from the anode and the cathode respectively, and their fast transport and recombination in the emissive layer.\(^4\)\(^,\)\(^5\) To achieve high device efficiency, it is necessary that both electrons and holes are efficiently injected.\(^5\)\(^,\)\(^6\) Therefore, substantial improvements in the device efficiency have been obtained upon modification of the anode,\(^7\)\(^-\)\(^9\) by the introduction of low-work function cathodes,\(^10\) and by using hole and electron injecting/transporting layers.\(^11\)\(^-\)\(^14\) Efficient injection of electrons from the cathode to emissive conjugated polymers plays an important role in improving the device efficiency and stability. For most conjugated polymers, hole injection is more favorable than electron injection.\(^11\)\(^,\)\(^15\) Therefore, low work-function metals such as Ba and Ca are the widely utilized cathode materials to facilitate efficient electron injection. However, those metals are very sensitive to moisture and oxygen and probably form detrimental quenching sites near the interface between the emission layer (EML) and the cathode.

To overcome these problems, the cathode should be stable to environment, the environmentally stable high-work-function metals such as Al, Cu, Ag, and Au as the cathode has attracted extensive attention recently. However, electron injection from cathode is usually hindered by its high work-function. Therefore, use of a water- or alcohol-soluble electron injection layer (EIL) based on a conjugated polymer grafted with amino, ammonium salt, or diethanolamino groups has been demonstrated to allow the use of a high-work-function metal as the cathode.\(^16\)\(^-\)\(^23\) This is because interfacial dipole or space charge is formed between the emitting layer (EML) and the cathode that reduces the electron injection barrier. In addition, crown ether groups may be expected to serve the same purpose.
Crown ethers are a special class of ether able to form stable complexes with alkali, alkaline-earth, and transition-metal ions. Chen et al. first reported the use of water/methanol-soluble polyfluorene grafted with 18-crown-6 as the electron-injection layer (EIL) for deep-blue-emission PLEDs, allowing the use of environmentally stable Al as the cathode.

Moreover, ethylene glycol groups also show good solubility in highly polar solvents and poly(ethylene glycol)-based surfactants demonstrate performance enhancement for PLEDs using high-work-function metal aluminum as cathode. Among the typical electron-affinitive materials, aromatic 1,2,4-triazolyl based derivatives show good thermal and chemical stabilities, leading to their common use as electron injection/transport and hole-blocking materials in LEDs. However, their solubility in solvents are quite limited, especially in mixture of water and alcohol. Solubility in water or alcohol is a requirement for electron-injection material to be spin-coated on top of emission layer. Otherwise, subsequent solvents will damage the emission layer by partial dissolution. By introducing ethylene glycol ether groups to aromatic 1,2,4-triazolyl core, its solubility in alcohol can be further enhanced.

Recently, most of the water- or alcohol-soluble electron injection materials mainly based on polymers are developed and demonstrated. Nonetheless, a few researches focus on small molecule have been reported. In particular, small-molecular-weight materials have received interest due to their easy purification by re-crystallization or column chromatographic techniques, and mono-disperse with well-defined chemical structures, and synthetically well-reproducibility. In this study, we propose the use of a alcohol-soluble and small-molecule 1,2,4-triazole-based 3OTAZ with diethylene glycol monoethyl ether groups as the EIL in PLEDs with HY-PPV (PDY-132, Merck) as emitting layer (EML). The solubility in highly polar solvents (e.g., alcohol) provided by diethylene glycol monoethyl ether can prevent dissolution of the EML having a thin EIL atop it, and the
1,2,4-triazole parts with electron-affinitive ability to reduce the electron-injection barrier from a stable metal cathode (e.g., Al, Ag or Au) and to facilitate electron injection. When the 3OTAZ was inserted between the emitting layer and the Al cathode as an EIL, the device efficiency was efficiently enhanced. The maximum luminance, maximum current efficiency and maximum luminous power efficiency were 2970 cd/m², 0.91 cd/A, and 0.34 lm/W, respectively, which were greatly superior to those without electron injection layer (230 cd/m², 0.02 cd/A, 0.006 lm/W). The results indicate that the 3OTAZ is a promising electron injection layer for high performance PLEDs with high work function Al cathode.

**Experimental Section**

**Materials**

N,N-Dimethylformamide (DMF), methyl alcohol, di(ethylene glycol)monoethyl ether, chloroform, isopropyl alcohol, dimethyl sulfoxide, acetone, and acetonitrile were purchased from Tedia Chemicals and used as received. Hydrazine hydrate (Lancaster), 4-fluoroaniline (Alfa Aesar), 4-fluorobenzoic chloride (Acros), N-methyl-2-pyrrolidone (Janssen), phosphorus pentachloride (RDH), NaH (Acros), ethyl alcohol (Echo), N,N'-dimethylaniline (Acros), toluene (Echo), potassium bromide (Showa), ferrocene (Acros), tetra-n-butylammonium perchlorate (TCI), acetone (J. T. Backer) were from commercial sources and used without further purification. Hole-injection material poly(3,4-ethylendioxythiophene-polystyrenesulfonate (PEDOT:PSS) and yellow-emitting material Livilux PDY-132 (Super Yellow; HY-PPV) were acquired from Bayer and Merck, respectively.

**Measurements**

All new synthesized compounds were identified by \(^1\)H NMR, \(^{13}\)C-NMR, FT-IR spectra, elemental analysis (EA) and Mass spectroscopy (MS). The \(^1\)H and \(^{13}\)C NMR spectra were obtained on a Bruker AMX-400 MHz spectrometer, with the chemical shifts reported in
ppm using tetramethylsilane (TMS) as an internal standard. The FT-IR spectra were measured as KBr disk on a Fourier transform infrared spectrometer, model 7850 from Jasco. The elemental analysis was carried out on a Heraus CHN-Rapid elemental analyzer. Thermogravimetric analysis (TGA) of samples was performed under nitrogen atmosphere at a heating rate of 10 °C/min using a PerkinElmer TGA-7 thermal analyzer. Thermal transition properties of samples were investigated using a differential scanning calorimeter (DSC), Mettler Toledo DSC 1 Star System, under nitrogen atmosphere at a heating rate of 10 °C/min. Absorption and photoluminescence (PL) spectra were measured with a Jasco V-550 spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. Cyclic voltammograms were recorded with a voltammetric analyzer (model CV-50W from Bioanalytical Systems, Inc.) at room temperature under nitrogen atmosphere. The measuring cell was made up of a polymer-coated ITO glass as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire as the auxiliary electrode. The electrodes were immersed in acetonitrile containing 0.1 M (n-Bu)_4NClO_4 as electrolyte. The energy levels were calculated using the ferrocene (FOC) value of -4.8 eV with respect to vacuum level, which is defined as zero. An atomic force microscope (AFM), equipped with a Veeco/Digital Instrument Scanning Probe Microscope (tapping mode) and a Nanoscope IIIa controller, was used to examine the morphology and to estimate the thickness and root-mean-square (rms) roughness of deposited films. The film thicknesses of electron injection and emitting layers were measured by a surface profiler (α-step 500).

**Synthesis of Electron-Injection Material 3OTAZ (Scheme 1)**

A mixture of 3,4,5-tris(4-fluorophenyl)-4H-1,2,4-triazole (3: 1.45 g, 4.11 mmol), di(ethylene glycol) monoethyl ether (2.42g, 18 mmol), and NaH 50% (0.86 g, 18 mmol) with DMF (10 mL) as solvent was stirred at 130 °C for 24 h under a nitrogen atmosphere. The mixture was poured into a large amount of distilled water. The appearing precipitates were collected by filtration and then recrystallized from DMSO and water to afford
compound **3OTAZ** (Yield: 80.1%). $^1$H-NMR (DMSO-d$_6$, ppm): δ 7.31~7.28 (m, 6H, Ar-H), 7.00 (d, 2H, $J = 9.0$ Hz, Ar-H), 6.91 (d, 4H, $J = 9.0$ Hz, Ar-H), 4.10~4.06 (m, 6H, -CH$_2$-), 3.74~3.69 (m, 6H, -CH$_2$-), 3.58~3.54 (m, 6H, -CH$_2$-), 3.49~3.46 (m, 6H, -CH$_2$-), 3.44~3.39 (m, 6H, -CH$_2$-), 1.07 (t, 9H, -CH$_3$). $^{13}$C-NMR (DMSO-d$_6$, ppm): δ 159.43, 159.01, 154.13, 129.89, 129.70, 127.81, 119.72, 115.47, 114.55, 70.13, 70.08, 69.33, 68.96, 67.37, 65.68, 40.20, 40.03, 39.86, 39.70, 39.53, 39.36, 39.20, 15.22. Anal. Calcd. for C$_{38}$H$_{51}$N$_3$O$_9$: C, 65.78%; H, 7.41%; N, 6.06%. Found: C, 66.11%; H, 7.72%; N, 5.86%.

![Scheme 1. Synthetic procedures of 3OTAZ.](image)

## Fabrication of Polymer Light-Emitting Diodes

Multilayer polymer light-emitting diodes (PLEDs), with a structure of ITO/PEDOT:PSS/HY-PPV/3OTAZ/Al, were fabricated by the wet processes for the
investigation of optoelectronic characteristics. The glass substrate coated with an ITO conductive layer was used as the anode, the poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS, Bayer) as the hole-injection layer, the Livilux PDY-132 (HY-PPV, Merck) as the light-emitting layer, the 3OTAZ as the electron-injection layer, and aluminum as the metal cathode. The ITO-coated glasses were washed successively in an ultrasonic bath of neutral cleaner/de-ionized water mixture, de-ionized water, acetone and 2-propanol, followed by treatment in a UV-ozone chamber. A thick hole-injection layer of PEDOT:PSS was spin-coated on top of the cleaned ITO glass and annealed at 423 K for 900 s in a dust-free atmosphere. The emitting layer (EML) was deposited by spin-coating the HY-PPV solution (6 mg/1 ml toluene) on top of the PEDOT:PSS layer at 6000 rpm and annealed at 65 °C for 25 min to remove the residual solvent. The electron-injection layer was cast on top of the EML by the spin-coating (1 mg/ml in ethanol) of the 3OTAZ. Finally, the aluminum (90 nm) was deposited as the cathode by thermal evaporation at about 1 \times 10^{-6} \text{Torr}. The current-luminance-voltage (I-L-V) characteristics of the devices were recorded using a combination of a Keithley power source (model 2400) and an Ocean Optics usb2000 fluorescence spectrophotometer. Current efficiency and luminous power efficiency were calculated from the I-L-V characteristics. The fabrication of the devices was done in ambient conditions, with the following performance tests conducted in a glove-box filled with nitrogen.

**Results and discussion**

**Characterization of Electron-injection Material 3OTAZ.**

The electron-injection material 3OTAZ was synthesized from 3,4,5-tris(4-fluorophenyl)-4H-1,2,4-triazole (3) and 2-(2-ethoxyethoxy)ethanol by the nucleophilic substitution reaction (Scheme 1). The chemical structure of 3OTAZ had been well characterized by $^1$H NMR spectra and elemental analysis (in Supporting Information),
whereas its optical properties were investigated by absorption spectroscopy (UV/Vis) and photoluminescence spectroscopy (PL). Glass transition temperatures ($T_g$) and thermal decomposition temperatures ($T_d$) (at 5 wt% loss) of 3OTAZ were evaluated with differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), respectively. Cyclic voltammetry (CV) was used to measure onset reduction and oxidation potentials of 3OTAZ film, which in turn were used to estimate the LUMO and HOMO levels respectively.

**Thermal Properties**

Glass transition temperatures ($T_g$) and thermal decomposition temperatures ($T_d$) (at 5 wt% loss) of 3OTAZ were evaluated with differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) respectively, with the representative data summarized in Table 1. The melting point ($T_m$) of 3OTAZ was observed at 67 °C (Figure S4 in SI), but no obvious glass transition temperature ($T_g$) and crystallization temperature ($T_c$) was detected between 30°C and 300 °C. This is due to three diethylene glycol ether groups of 3OTAZ which effectively prevent close packing between the molecules. In addition, thermal decomposition temperature at 5% weight loss was quite high (376 °C) (Figure 1), indicating that 3OTAZ is thermally stable to be applied in PLEDs.
Figure 1. Thermogravimetric curves of 3OTAZ at a heating rate of 10 °C/min under nitrogen atmosphere.
Table 1. Thermal, optical and electrochemical properties of 3OTAZ.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_m^a/T_d^b$ ($^\circ$C)</th>
<th>UV-vis $\lambda_{max}$/PL $\lambda_{max}$ (nm)</th>
<th>$E_{onset(ox)}$ vs. FOC (V)$^e$</th>
<th>$E_{onset(red)}$ vs. FOC (V)$^e$</th>
<th>$E_{HOMO}/E_{LUMO}$ (eV)$^f$</th>
<th>$E_{g}^{el}$/ $E_{g}^{opt}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3OTAZ</td>
<td>67/376</td>
<td>272$^c$ (286, 347, 375)$^d$/356$^c$ (358)$^d$</td>
<td>1.06</td>
<td>-1.92</td>
<td>-5.86/-2.88</td>
<td>2.98/3.62</td>
</tr>
</tbody>
</table>

$^a$ Melting point determined by DSC measurement.

$^b$ The decomposition temperature at 5 wt% loss was measured by TGA at a heating rate of 10 $^\circ$C/min under nitrogen.

$^c$ In ethanol (1×10$^{-5}$M).

$^d$ film state.

$^e$ $E_{FOC} = 0.49$ V vs. Ag/AgCl.

$^f$ $E_{HOMO} = -(E_{onset(ox)}, FOC + 4.8)$ eV; $E_{LUMO} = -(E_{onset(red)}, FOC + 4.8)$ eV.

$^g$ $E_{g}^{el} = |LUMO-HOMO|$: electrochemically estimated band-gap.

$^h$ $E_{g}^{opt} = 1240/\lambda_{onset(abs. spectrum)}$ (nm): optically estimated band-gap.
Optical Properties

Figure 2 illustrates the absorption and photoluminescence (PL) spectra of 3OTAZ in solution (ethanol) and as film spin-coated from ethanol solution, with the characteristic optical data summarized in Table 1. The absorption maxima of 3OTAZ are peaked at ca. 272 nm and 286 nm (with shoulders at 347 nm and 375 nm) in ethanol and as film, respectively. The major absorption of 3OTAZ (ca. 272 nm and 286 nm) can be attributed to the $\pi-\pi^*$ transitions of 1,2,4-triazole moieties, whereas the shorter-wavelength absorptions in the film state (ca. 347 nm and 375 nm) is probably originated from the $n-\pi^*$ transitions between diethylene glycol monoethyl ether moieties and 1,2,4-triazole core. The PL spectra of 3OTAZ in solution and solid state locate at ca. 356 nm and ca. 358 nm, respectively. The absorption and PL maxima of 3OTAZ in solid state (286 nm and 358 nm) are red-shifted slightly relative to solution state (272 nm and 356 nm), probably due to excimer formation via intra- or inter-chain interactions.

![Figure 2](image)

**Figure 2.** Absorption and photoluminescence spectra of 3OTAZ in ethanol solution ($\lambda_{ex} = 272$ nm) and film state ($\lambda_{ex} = 286$ nm).

Electrochemical Properties
Cyclic voltammetry (CV) was employed to investigate the electrochemical properties of 3OTAZ. The cyclic voltammograms of 3OTAZ dissolved in 0.1M n-Bu$_4$NCIO$_4$ are shown in Figure 3, with the representative electrochemical data summarized in Table 1. The HOMO and LUMO energy levels were estimated by the equations: $E_{\text{HOMO}}(\text{eV}) = -(E_{\text{ox,FOC}} + 4.8)$ and $E_{\text{LUMO}}(\text{eV}) = -(E_{\text{red,FOC}} + 4.8)$, where $E_{\text{ox,FOC}}$ and $E_{\text{red,FOC}}$ are the onset oxidation and onset reduction potentials, respectively, relative to the ferrocene/ferrocenium couple whose energy level is already known (-4.8 eV). The HOMO and LUMO energy levels of 3OTAZ were estimated to be -5.86 eV and -2.88 eV respectively, as well as electrochemical band-gap ($E_g^{\text{el}}$) being 2.98 eV.

![Cyclic voltammogram of 3OTAZ dissolved in acetonitrile with 0.1M n-Bu$_4$NCIO$_4$. Working electrode: glassy carbon, scan rate: 100 mV/s.](image)

**Figure 3.** Cyclic voltammogram of 3OTAZ dissolved in acetonitrile with 0.1M n-Bu$_4$NCIO$_4$. Working electrode: glassy carbon, scan rate: 100 mV/s.

On the other hand, the optical band-gap ($E_g^{\text{opt}}$) was estimated to 3.62 eV from the main onset absorption wavelength (343 nm) of 3OTAZ in the film state (Figure 2). The energy band-gaps obtained by optical method and cyclic voltammetry were 2.98 eV and 3.62 eV, respectively. Electrochemically-estimated band-gap ($E_g^{\text{el}}$), calculated using $E_g^{\text{el}} = |\text{LUMO} - \text{HOMO}|$, is slightly different from optical band-gap ($E_g^{\text{opt}}$) obtained from onset absorption.
The electrochemical band-gap (\(E_g^{el}\)) is the energy difference between the LUMO and HOMO levels, which in turn are estimated from the onset oxidation and reduction potentials, respectively. However, oxidation and reduction may start from different parts of a molecule which is composed of electron-donating and electron-withdrawing groups. Therefore, the discrepancy between the band-gaps determined electrochemically (\(E_g^{el}\)) and optically (\(E_g^{opt}\)) is probably due to their different techniques to estimate the gaps. Due to 3OTAZ is comprised of 1,2,4-triazoly core and three diethylene glycol monoethyl ether, oxidation may start from the electron-donating diethylene glycol monoethyl ether parts, and reduction may start from the 1,2,4-triazoly core of 3OTAZ.

**Electroluminescent Enhancement of PLEDs by inserting 3OTAZ**

According to the energy band diagrams depicted in Figure 4, the energy barrier between aluminum (A1) and HY-PPV (2.5 eV) is larger than that between PEDOT:PSS and HY-PPV (0 eV). Moreover, holes are usually more readily transported than electrons in conjugated materials, leading to reduced recombination ratio of holes and electrons. Similar nonmatching energy barriers for electrons and holes are also apparent for the HY-PPV based device (Figure 4). However, the charge injection/transport imbalance in HY-PPV can be alleviated by inserting the electron injection and hole-blocking layer 3OTAZ in which both LUMO and HOMO energy levels are lower than those of HY-PPV. The lowered LUMO and HOMO levels give rise to enhanced electron injection/transport and hole-blocking, respectively, resulting in more balanced charges recombination.
Multi-layer polymer light-emitting diodes (PLEDs) with a configuration of ITO/PEDOT:PSS/EML (HY-PPV)/EIL/Al (90 nm) were fabricated to investigate their electroluminescent characteristics. In this work, we propose the use of a water/alcohol-soluble 3OTAZ as electron injection layer (EIL) in a PLED with HY-PPV as the EML. The EIL was deposited on top of the EML by spin-coating of 3OTAZ solution (1 mg 3OTAZ/ml) using various spin speed (1000, 2000 and 3000 rpm). Current density–luminance–voltage (J–L–V) and luminous efficiency–power efficiency–current density (LE–PE–J) characteristics of the devices are shown in Figure 5 and Figure 6-7, with the corresponding optoelectronic data summarized in Table 2. The device performance is effectively enhanced by inserting the electron-injection layer (3OTAZ) between emitting layer (HY-PPV) and Al cathode.

Maximum luminance and current efficiency of devices were greatly increased from 230 cd/m² and 0.02 cd/A (0.006 lm/W) to 2970 cd/m² and 0.91 cd/A (0.34 lm/W), respectively, by inserting the electron-injection layer (EIL: 3OTAZ with 3000 rpm spin speed) between emitting layer and Al cathode (Figure 5 and Figure 6-7). Although the performance
enhancement is inferior to that obtained with a conventional LiF/Al cathode, the 3OTAZ
effectively promote the device performance. The performance enhancement is probably
attributed to the hole-blocking and improved electron injection effect of 3OTAZ that raises
charges recombination ratio. The HOMO level of 3OTAZ (-5.86 eV) is much lower than
that of emitting layer HY-PPV (-5.0 eV), resulting in blocking and accumulation of holes in
the HY-PPV layer close to the interface. Moreover, the lower LUMO level of 3OTAZ
(-2.88 eV) than emitting layer HY-PPV (-2.8 eV) promotes electron injection (Figure 4).
Therefore, holes will readily combine with electrons passing through the interface to
increase the recombination ratio.

As shown in Table 2, the device with 3OTAZ as EIL spin-coated at 3000 rpm reveals
the best performance. Moreover, the turn-on voltages of the device decreases to 4.2 V which
is much lower than 8.3 V obtained for that without 3OTAZ as EIL. The electroluminescent
enhancement is ascribed to effectively promoted electron injection/transport with 3OTAZ as
EIL that leads to higher charges recombination ratio. However, more homogeneous surface
morphology of the EIL spin-coated at 3000 rpm (Figure S6 in SI: RMS roughness = 1.65 nm)
also contributes to the performance improvement. In addition, the 1931 CIE coordinates (x,
y) of the EL emission only shift slightly from (0.35, 0.60) to (0.41, 0.57) when the 3OTAZ
is inserted as EIL (Table 2), indicating that the emission of all devices is exclusively
originated from HY-PPV.
Figure 5. Luminance versus voltage and current density versus voltage characteristics of PLEDs. Device structure: ITO/PEDOT:PSS/HYPPV/3OTAZ/Al.

Table 2. Optoelectronic Properties of the Light-emitting Diodes

<table>
<thead>
<tr>
<th>EIL</th>
<th>Thickness of EIL (nm)</th>
<th>$V_{on}$ (V)$^b$</th>
<th>$L_{max}$ (cd/m$^2$)$^c$</th>
<th>$CE_{max}$ (cd/A)$^d$</th>
<th>$LPE_{max}$ (lm/W)$^e$</th>
<th>CIE (x, y)$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>—</td>
<td>8.2</td>
<td>230</td>
<td>0.02</td>
<td>0.006</td>
<td>(0.35, 0.60)</td>
</tr>
<tr>
<td>1000 rpm</td>
<td>87</td>
<td>4.8</td>
<td>1140</td>
<td>0.43</td>
<td>0.16</td>
<td>(0.40, 0.58)</td>
</tr>
<tr>
<td>2000 rpm</td>
<td>79</td>
<td>4.2</td>
<td>2670</td>
<td>0.71</td>
<td>0.27</td>
<td>(0.41, 0.57)</td>
</tr>
<tr>
<td>3000 rpm</td>
<td>60</td>
<td>4.3</td>
<td>2970</td>
<td>0.91</td>
<td>0.34</td>
<td>(0.41, 0.57)</td>
</tr>
</tbody>
</table>

$^a$ [ITO/PEDOT:PSS/HY-PPV (~80 nm)/EIL/Al (90nm)].

$^b$ Turn-on voltage at 10 cd/m$^2$.

$^c$ Maximum luminance.

$^d$ Maximum current efficiency.

$^e$ Maximum luminous power efficiency.

$^f$ The 1931 CIE coordinate at maximum luminance.
Figure 6. Current efficiency versus current density characteristics of PLEDs. Device structure: ITO/PEDOT:PSS/HYIPPV/3OTAZ/Al.

Figure 7. Luminous power efficiency versus current density characteristics of PLEDs. Device structure: ITO/PEDOT:PSS/HY-PPV/3OTAZ/Al.

To clarify the hole-blocking effect of EIL (3OTAZ), hole-only devices
ITO/PEDOT:PSS/HYIPPV/EIL/Au (100 nm) were fabricated to investigate their current density versus bias characteristics. As shown in Figure 8, the curve shifts horizontally to higher bias after the insertion of 3OTAZ as EIL, indicating diminished current density under the same bias. The device using 3OTAZ (spin speed: 1000, 2000 and 3000 rpm) as EILs reveal the similar current density, indicating that the hole-blocking effect is induced by inserting 3OTAZ. However, the voltage-induced current densities are still lower than that of the device without EIL. Therefore, more balanced charges injection and transport was achieved by inserting EIL 3OTAZ which adjust hole-blocking.

![Current density versus voltage characteristics](image)

**Figure 8.** Current density versus voltage characteristics of hole-only PLEDs. Device structure: ITO/PEDOT:PSS/HY-PPV/EIL/Au.

To demonstrate the electron injection ability of the EIL (3OTAZ), electron-only devices [Glass/PEDOT:PSS/Ag (100 nm)/HY-PPV/EIL/A1 (90 nm)]\textsuperscript{33,34} were fabricated to
investigate their current density versus bias characteristics (Figure 9). The current density (under the same bias) is raised by the EILs, especially in the devices using the 3OTAZ (spin speed: 3000 rpm) as EIL reveal the highest current density. This is attributed to enhancement in electron injection/transport by the 3OTAZ. This suggests that the 3OTAZ (spin speed: 3000 rpm) is the most effective EIL to promote electron injection/transport and more balance charges injection and transport.

![Figure 9](image.png)

**Figure 9.** Current density versus voltage characteristics of electron-only PLEDs. Device structure: ITO/PEDOT:PSS/Ag/HYIPPV/EIL/Al.

Photovoltaic (PV) measurements were conducted to elucidate that addition of 3OTAZ plays crucial role in promoting electron injection in the PLEDs. When the anode is kept identical (ITO/PEDOT:PSS), the open-circuit voltage ($V_{oc}$) is primarily determined by effective work-function of the cathode, which reflects the electron-injection ability of the EIL materials.$^{11,35}$ The $V_{oc}$ was 1.32 V for the device based on HY-PPV without EIL, respectively, which was increased to 1.45 V when the 3OTAZ was inserted as the EIL
(Figure 10). Higher $V_{oc}$ means that the built-in potential (the difference in work function between anode and cathode) across its anode/EML/cathode junction has been increased. Therefore, a drop in the work function of EIL/Al cathode (or generation of interfacial dipoles at the EIL/metal junction) has been realized by inserting the EIL. Lower work function of cathode usually facilitates electron injection. Accordingly, the significant performance enhancement in devices using the 3OTAZ as EIL should be mainly due to enhanced electron-injection ability. Current results indicate that aromatic 1,2,4-triazole-based 3OTAZ with diethylene glycol monoethyl ether groups is not only an effective hole-blocking material but also a promising stable cathode modifier in promoting electron injection and device performance.

![Graph](image)

**Figure 10.** Photovoltaic measurements of PLEDs using 3OTAZ as electron injection layer under illumination from a solar simulator (Newport, Oriel class A, 91160A) at 100% sun (AM1.5, 100 mW/cm²). Device structure: ITO/PEDOT:PSS/HY-PPV/EIL/Al.

**Conclusion**

We have presented a novel aromatic 1,2,4-triazole-based 3OTAZ with diethylene glycol monoethyl ether groups as electron-injection layer (EIL) and hole-blocking layer for
fabrication of multilayer PLEDs by spin-coating process. The 3OTAZ was a highly efficient EIL to more balance charge injection/transport. The devices based on HY-PPV as emission layer with 3OTAZ (spin speed: 3000 rpm) as EIL (ITO/PEDOT:PSS/HY-PPV/EIL/Al) revealed the best device performance. Maximum luminance and current efficiency of devices were 2970 cd/m$^2$ and 0.91 cd/A (0.34 lm/W), respectively, which were superior to those without electron injection layer [230 cd/m$^2$ and 0.02 cd/A (0.006 lm/W)]. In addition, the turn-on voltage of the device was decreased to 4.2 V which is much lower than 8.3 V obtained for those without 3OTAZ as EIL. The electron- and hole-only devices and their open circuit voltages ($V_{oc}$) had been investigated to clarify their charges injection/transport abilities and the influence of 3OTAZ in electroluminescence. The performance enhancement has been attributed to promoted electron injection/transport and hole-blocking effect by the inserted 3OTAZ. Current results demonstrate that 3OTAZ is an effective electron injection/transport material applicable to optoelectronic devices.

**Supporting Information**
Synthesis and characterization of monomers, the COSY and NOESY NMR spectra of 3OTAZ, and surface AFM images of 3OTAZ thin film.

**Acknowledgment**
This research received funding from the Headquarters of University Advancement at the National Cheng Kung University, which is sponsored by the Ministry of Education, Taiwan, ROC.

**References and Notes**


(22) X. Xu, B. Han, J. Chen, J. Peng, H. Wu, Y. Cao, Macromolecules 2011, 44, 4204.


