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# Introduction

For more than two decades, polymer light-emitting diodes (PLEDs)<sup>1-3</sup> have attracted continued 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.<sup>4,5</sup> To achieve high electroluminescence efficiency, it is necessary that both electrons and holes are efficiently injected.<sup>5,6</sup> Therefore, substantial improvements in the device efficiency have been obtained upon modification of the anode,<sup>7-9</sup> 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 the emissive conjugated polymers plays an important role in improving the device efficiency and stability. For most existing conjugated polymers, electron injection is more difficult than hole injection.11,15 It is well-known that

# Synthesis and characterization of triple-azacrown ethers containing fluorene-cored derivatives: application as electron injection layer for significantly enhanced performance of PLEDs<sup>+</sup>

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To enhance electroluminescence of polymer light-emitting diodes (PLEDs) using an environmentally stable aluminum cathode, we designed a novel water/alcohol-soluble electron injection material, **FTC**, composed of a fluorene core and triple azacrown ether terminals. **FTC** significantly enhances the emission performance of PLEDs [ITO/PEDOT:PSS/EML/EIL/AI] when used as the electron injection layer (EIL), especially in the presence of metal carbonates and metal acetates. The metal carbonate-doped devices showed the best performance due to their higher dissociation rate than metal acetates. In particular, the device using K<sub>2</sub>CO<sub>3</sub> doped-**FTC** as the electron injection layer (EIL) exhibited significantly enhanced performance compared to the device without an EIL. For the device based on PF-Green-B as the emitting layer, the performance was significantly enhanced to 17 460 cd m<sup>-2</sup>, 21.58 cd A<sup>-1</sup>, and 12.42 lm W<sup>-1</sup>, respectively, from 1220 cd m<sup>-2</sup>, 0.72 cd A<sup>-1</sup>, and 0.27 lm W<sup>-1</sup> for the non-**FTC** device. Using HY-PPV as the emitting layer, the device performance was also significantly enhanced to 10 990 cd m<sup>-2</sup>, 6.93 cd A<sup>-1</sup>, and 5.27 lm W<sup>-1</sup>, respectively, from 680 cd m<sup>-2</sup>, 0.07 cd A<sup>-1</sup>, and 0.03 lm W<sup>-1</sup> for the non-EIL device. The results indicate that **FTC** with metal cations is an excellent electron injection candidate for the performance enhancement of PLEDs with a high work function Al cathode.

electron injection is dependent on the energy barrier height between the emitting layer and the cathode. Therefore, low work-function metals such as Ba and Ca are widely utilized as cathode materials to facilitate efficient electron injection. However, these metals are not stable in air, and they may sometimes react with and diffuse into organic materials, leading to the deterioration of the device.

For development of PLEDs industrialization, the cathode must be stable to environmental conditions, and the use of environmentally stable high-work-function metals such as Al, Cu, Ag, and Au as the cathode has attracted extensive attention recently. 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 to the above hydrophilic groups, 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.<sup>24,25</sup> Chen et al. first reported the use of water/methanol-soluble polyfluorene grafted with 18-crown-6 chelating to K<sup>+</sup> as the electron-injection layer (EIL) for deepblue-emission PLEDs, allowing the use of environmentally

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Synthesis and characterization of monomers, the <sup>1</sup>H NMR spectra, and thermal, optical, electrochemical and optoelectronic properties of **FTC**, and the proposed chemical structure of doped-**FTC**. See DOI: 10.1039/c3tc31301h

stable Al as the cathode.<sup>26</sup> The device exhibited the highest performance reported to date for a deep-blue-emission PLED based on a conjugated polymer as the emitting layer, with a brightness of 54 800 cd m<sup>-2</sup> and an external quantum efficiency of 5.42%. An azacrown ether is a crown ether that has nitrogen donor atoms as well as oxygen donor atoms to coordinate to the metal iron. The nitrogen atoms in an azacrown ether should play an important role in coordination with metal cations. This means that it can be a more effective EIL than a crown ether when applied in PLEDs.

Recently, most water/alcohol-soluble electron injection materials that have been developed and demonstrated are mainly based on polymers.<sup>16-23,26</sup> Nonetheless, a few studies focused on small molecules have been reported. In particular, small-molecular-weight materials have received interest due to their easy purification by recrystallization or column chromatographic techniques, their monodispersity with well-defined chemical structures, and their good synthetic reproducibility. In addition, among the typical fluorescent materials, fluorene-based derivatives show good thermal and chemical stabilities, exhibit wide energy band gaps, and have high photoluminescence (PL) efficiencies (60-80%) in solution and solid state.27-29 Moreover, vinyl groups have also been introduced between fluorene-cored and triple-azacrown ethers, to extend the conjugation of monofluorene to achieve more suitable LUMO and HOMO energy levels. To the best of our knowledge, little attention has been paid to the effects of different metal cations and different anionic groups on electron injection layers.

In this study, we propose the use of a water/alcohol-soluble small-molecule fluorene derivative, FTC, doped with M<sub>2</sub>CO<sub>3</sub> (M = Na, K, Cs) and  $CH_3COOM$  (M = Na, K) as the EIL in PLEDs with PF-Green-B (Dow Chemical LUMATION<sup>30,31</sup>) and HY-PPV (PDY-132, Merck<sup>32,33</sup>) as the emitting layer (EML). Moreover, to the best of our knowledge this is the first investigation into the doping effect of different counter anions (CO<sub>3</sub><sup>-</sup> and CH<sub>3</sub>COO<sup>-</sup>) in the electron injection layer. The solubility in highly polar solvents (e.g., water or alcohol) provided by the azacrown can prevent dissolution of the EML having a thin EIL atop it, and the interaction of  $M^+$  (M = Na, K, Cs) with the azacrown allows the M<sup>+</sup> ion to act similarly to a metallic state in reducing the electron injection barrier from a stable metal cathode (e.g., Al, Ag or Au) and facilitating electron injection. When FTC binding M<sup>+</sup> (M = Na, K, Cs) was inserted between the emitting layer and the Al cathode as an EIL, the device efficiency was significantly enhanced. Particularly, the device using FTC doped with K<sub>2</sub>CO<sub>3</sub> as the electron injection layer showed the highest performance. For the devices based on PF-Green-B, the maximum luminance, maximum current efficiency and maximum luminous power efficiency were 17 460 cd m  $^{-2}$  , 21.58 cd  $A^{-1}$  , and 12.42  $\rm{lm}~W^{-1}$  , respectively, which were significantly superior to those without the electron injection layer (1220 cd  $m^{-2}$ , 0.72 cd  $A^{-1}$ , and  $0.27 \text{ lm W}^{-1}$ ). For the devices based on HY-PPV, the maximum luminance, maximum current efficiency and maximum luminous power efficiency were 10 990 cd m<sup>-2</sup>, 6.93 cd A<sup>-1</sup>, and 5.27  $\text{Im W}^{-1}$ , respectively, which were also much higher than those without the electron injection layer. The results indicate

that **FTC** with metal carbonates and metal acetates was an excellent electron injection layer for high performance PLEDs with a high work function Al cathode.

## **Experimental section**

#### Materials

All reagents and solvents, unless otherwise specified, were obtained from Aldrich, Acros, Showa, and J. T. Backer and were used as received. Poly(3,4)-ethylendioxythiophene–polystyrenesulfonate (PEDOT:PSS) was obtained from Bayer, green-emitting polyfluorene derivative (PF-Green-B) was obtained from Dow Chemical Company (Lumation®), and yellow-emitting material HY-PPV was obtained from Merck (Super yellow, Livilux PDY-132).

#### Measurements

All new synthesized compounds were identified by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis (EA). The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AMX-400 MHz FT-NMR, with the chemical shifts reported in ppm using tetramethylsilane (TMS) as an internal standard. The elemental analysis was carried out on a Heraeus CHN-Rapid elemental analyzer. Absorption and photoluminescence (PL) spectra were measured on a Jasco V-550 spectrophotometer and a Hitachi F-4500 spectrofluorometer, respectively. Cyclic voltammograms were measured with a voltammetric apparatus (model CV-50W from BAS) equipped with a three-electrode cell. The cell was made up of FTC-coated glassy carbon 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)<sub>4</sub>NClO<sub>4</sub> as the electrolyte. The energy levels were calculated using the ferrocene (FOC) value of -4.8 eV with respect to the vacuum level, which is defined as zero.

#### Synthesis of electron injection material FTC (Scheme 1)

A mixture of 4-(monoaza-15-crown-5)benzaldehyde (compound 4: 3.36 g, 10.4 mmol) and 2,4,7-tri[methylene(triphenylphosphonium bromide)]-9,9-dihexylfluorene (compound 6: 1.6 g, 1.1 mmol) in dried ethanol (20 ml) was added dropwise to sodium ethoxide (3.4 g, 10.4 mmol) and stirred at room temperature overnight under a nitrogen atmosphere. The mixture was extracted with chloroform and the combined organic layer was dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: acetone : *n*-hexane = 1 : 1, EA) (0.51 g, 34.5%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, TMS, 25 °C): δ 7.88-7.86 (d, 1H, Ar-H), 7.70-7.66 (d, 1H, Ar-H), 7.6 (s, 1H, Ar-H), 7.54-7.42 (m, 8H, Ar-H), 7.38 (s, 1H, Ar-H), 7.20-6.98 (m, 5H, Ar-H), 6.76-6.68 (m, 6H, Ar-H), 3.80-3.53 (m, 60H, crown ether), 2.06-2.02 (t, 4H, -CH2-), 1.16-1.03 (m, 12H, -CH2-), 0.79-0.75 (m, 6H, -CH<sub>3</sub>-), 0.67-0.65 (m, 4H, -CH<sub>2</sub>-). Anal. calc. for C<sub>79</sub>H<sub>109</sub>N<sub>3</sub>O<sub>12</sub>: C, 73.40; H, 8.50; N, 3.25. Found: C, 73.42; H, 8.72; N, 3.11.

#### Fabrication of polymer light-emitting diodes

Multilayer polymer light-emitting diodes (PLEDs), with a structure of ITO/PEDOT:PSS/EML/EIL/Al, were fabricated by wet processes for the investigation of optoelectronic characteristics. A glass substrate coated with an ITO conductive layer was used as the anode, poly(3,4-ethylenedioxythiophene)polystyrenesulfonate (PEDOT:PSS, Bayer) was used as the hole injection layer, the green polyfluorene derivative (PF-Green-B, Dow Chemical) or Livilux PDY-132 (HY-PPV, Merck) was used as the light-emitting layer, FTC (or FTC in the presence of metal cations) was used as the electron injection layer, and Al was used 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. For the devices based on PF-Green-B, the light-emitting film was prepared by spin-coating the PF-Green-B solution (10 mg per 1 ml toluene) on top of the PEDOT:PSS layer at 2500 rpm and annealing at 65 °C for 25 min to remove the residual solvent. For the devices based on HY-PPV, the emitting layer (EML) was deposited by spincoating the HY-PPV solution (6 mg per 1 ml toluene) on top of the PEDOT:PSS layer at 6000 rpm and annealing at 65 °C for 25 min to remove the residual solvent. The electron injection layer was cast on top of the EML by spin-coating (3000 rpm) of FTC and M<sub>2</sub>CO<sub>3</sub> in a mixed solvent of de-ionized water and 2-propanol (v/v = 1 : 5). The ratio of FTC :  $M^+$  was fixed at 1 : 9 (azacrown :  $M^+ = 1 : 3$ ), and the concentration was 1 mg FTC per ml. Finally, the aluminum (100 nm) was deposited as the cathode by thermal evaporation at about 1  $\times$  10<sup>-6</sup> 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 FTC

The electron injection material **FTC** was synthesized from monoaza-15-crown-5 derivative (4) and 2,4,7-tri[methylene-(triphenylphosphonium bromide)]-9,9-dihexylfluorene (6) by the Wittig reaction (Scheme 1). The chemical structure of **FTC** has been well characterized by <sup>1</sup>H NMR spectra and elemental analysis, whereas its optical properties were investigated by absorption spectroscopy (UV-vis) and photoluminescence spectroscopy (PL). Cyclic voltammetry (CV) was used to measure the onset reduction and oxidation potentials of the **FTC** film, which in turn were used to estimate the LUMO and HOMO levels respectively. The thermal transitional properties of **FTC** were studied by differential scanning calorimetry (DSC).

The chemical shifts at 2.06–0.65 ppm are attributed to the protons on the long alkyl chains of **FTC** (Fig. 1). The protons have been further assigned using COSY spectra (Fig. S1 in ESI†). The chemical shifts of the protons belonging to the azacrown ether moieties are located at 3.80–3.53 ppm, in which the chemical shifts at 3.80–3.71 ppm are assigned to the protons symmetrically adjacent to the nitrogen atom. The chemical shifts at 3.65–3.53 ppm are attributable to the protons attached to the carbons of ether groups (C–O–C). The complex and multiple chemical shifts around 7.88–6.68 ppm are due to the signals of the protons belonging to the aromatic and vinylene parts of **FTC**. Due to the complexity of the spectrum, the assignment of individual protons has been assisted by two dimensional COSY and NOESY spectra (Fig. S2 and S3 in ESI†).

Homonuclear correlation spectroscopy (COSY) is used to identify spins which are coupled to each other. COSY spectra give information about pairs of protons that are J-coupled. This usually indicates that the protons are on adjacent carbons, e.g., 3 bonds away. NOESY (Nuclear Overhauser Effect Spectroscopy) spectra indicate proton-proton through space interactions via the NOE, which gives information about pairs of protons that are close in space (<5 Å apart). The chemical shifts at 2.06–0.65 ppm are attributed to the protons on the long chain of FTC by <sup>1</sup>H NMR. As demonstrated in the COSY spectrum (Fig. S1 in ESI<sup>†</sup>), there is an off-diagonal peak between 2.06 and 2.02 ppm and 0.67-0.65 ppm. The signal at 2.06-2.02 ppm is known to be due to the protons at position k, which indicates that the signal at 0.67–0.65 ppm is due to the protons at position l. Also, there is an off-diagonal peak between 0.67 and 0.65 ppm (position l) and 1.16-1.03 ppm, so the peak at 1.16-1.03 ppm is assigned to position m. From another off-diagonal peak between 1.16-1.03 ppm (position *m*) and 0.79–0.75 ppm, the peak at 0.79–0.75 ppm can be assigned as position n. The protons at positions k, l, m and *n* can be further confirmed by the integration of the  $^{1}$ H NMR spectrum.

For the aromatic part (Fig. S2 in ESI<sup>†</sup>), there is an off-diagonal peak between 7.88 and 7.86 ppm and 7.46–7.42 ppm; the former has been assigned as position *a*, hence the latter one can be attributed to position *b*. Another off-diagonal peak is found between 7.70 and 7.66 ppm and 7.20–6.98 ppm; the former doublet has been assigned as position *c*, so the latter chemical shift is due to the doublet of position *d*. According to the fact that linkage with a nitrogen atom usually results in electron rich protons and the integration of the chemical shifts at 6.76–6.68 ppm, these peaks are attributed to position *e* of the benzene rings. Hence, the off-diagonal peak between 6.76 and 6.68 ppm and 7.54–7.42 ppm is assigned to the signals of positions *e* and *f*. This is further verified by observing the corresponding offdiagonal peak in the NOESY spectra.

As shown in Fig. S3 (ESI<sup>†</sup>), an off-diagonal peak is observed between 7.70 and 7.66 ppm and 7.60 ppm, demonstrating the through space interaction between positions c and g. The offdiagonal peak between 7.60 ppm and 7.54–7.50 ppm is due to positions g and h of fluorene. As discussed above, by detailed analysis of the <sup>1</sup>H NMR, COSY and NOESY spectra, the protons of **FTC** have been assigned completely.



# Scheme 1 Synthetic procedure for FTC.

#### Thermal properties

Glass transition temperatures ( $T_g$ ) and thermal decomposition temperatures ( $T_d$ ) (at 5 wt% loss) of **FTC** were evaluated using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) respectively, with the representative data summarized in Table 1. The glass transition temperature ( $T_g$ ) and melting point ( $T_m$ ) of **FTC** were observed at 49 °C and 64 °C [Fig. S4 (ESI†)], respectively, but no obvious crystallization temperature ( $T_c$ ) was detected between 30 °C and 150 °C. The asymmetric structure of **FTC** and the twist of the 4-azacrown ether moiety relative to the fluorene plane effectively prevent close packing between the molecules. In addition, the thermal decomposition temperature at 5% weight loss was quite high (394  $^{\circ}$ C), indicating that **FTC** is thermally stable enough to be applied in PLEDs.

#### **Optical properties**

Fig. 2 illustrates the absorption and photoluminescence (PL) spectra of **FTC** in solution (CHCl<sub>3</sub>) and as a film spin-coated from  $CHCl_3$  solution, with the characteristic optical data summarized in Table 1. The absorption spectra of **FTC** in

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Fig. 1 <sup>1</sup>H NMR spectrum of compound FTC

solution and film state peak at *ca.* 416 nm and 424 nm, respectively. The absorption could be attributed to the  $n-\pi^*$  and  $\pi-\pi^*$  electronic transitions of the crown ether and the conjugated fluorenyl vinyl phenyl moiety. The PL spectra of **FTC** in solution and solid state are located at *ca.* 470 nm and *ca.* 535 nm, respectively. The solid state PL maximum of **FTC** is greatly red-shifted (65 nm) relative to the solution state, probably due to excimer formation *via* intra- or inter-chain interactions.

#### **Electrochemical properties**

Cyclic voltammetry (CV) was employed to investigate the electrochemical properties of **FTC**. The cyclic voltammograms are shown in Fig. S5 in the ESI,†,with the representative electrochemical data summarized in Table 1. HOMO and LUMO energy levels were estimated using the following equations:  $E_{\text{HOMO}}$  (eV) =  $-(E_{\text{ox,FOC}} + 4.8)$  and  $E_{\text{LUMO}}$  (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 levels is already known (-4.8 eV). The HOMO and LUMO energy levels of **FTC** were estimated to



Fig. 2 Absorption spectra and photoluminescence spectra of  $\ensuremath{\text{FTC}}$  in the film state and  $\ensuremath{\text{CHCl}_3}$  solution.

be -5.88 eV and -2.88 eV, respectively, and its electrochemical band gap ( $E_g^{el}$ ) was 3.0 eV.

On the other hand, the optical band gap  $(E_g^{opt})$  was estimated to 2.55 eV from the onset absorption wavelength of 486 nm

Table 1	able 1 Thermal, optical and electrochemical properties of FTC								
Material	$T_{g}^{a}/T_{m}^{b}/T_{d}^{c}$ (°C)	UV-vis $\lambda_{max}/PL \lambda_{max} (nm)$	$E_{\text{onset}(\text{ox})}$ vs. $\text{FOC}^{f}(V)$	$E_{\text{onset}(\text{red})}$ vs. $\text{FOC}^{f}(V)$	$E_{\rm HOMO}/E_{\rm LUMO}^{g}$ (eV)	$E_{\rm g}^{{\rm el}h}/E_{\rm g}^{{ m opt}i}$ (eV)			
FTC	49/64/394	$416^{d} \left(424\right)^{e} / 470^{d} \left(535\right)^{e}$	1.08	-1.92	-5.88/-2.88	3.00/2.55			

<sup>*a*</sup> Glass transition temperature determined by DSC measurement. <sup>*b*</sup> Melting point determined by DSC measurement. <sup>*c*</sup> The decomposition temperature at 5 wt% loss was measured by TGA at a heating rate of 10 °C min<sup>-1</sup> under nitrogen. <sup>*d*</sup> In chloroform (1 × 10<sup>-5</sup> M). <sup>*e*</sup> Film state. <sup>*f*</sup>  $E_{\text{FOC}} = 0.49$  V vs. Ag/AgCl. <sup>*g*</sup>  $E_{\text{HOMO}} = -(E_{\text{onset(ox),FOC}} + 4.8)$  eV;  $E_{\text{LUMO}} = -(E_{\text{onset(red),FOC}} + 4.8)$  eV. <sup>*h*</sup>  $E_{\text{g}} = |\text{LUMO} - \text{HOMO}|$ . <sup>*i*</sup>  $E_{\text{g}} = 1240/\lambda_{\text{onset(abs. spectrum)}}$  (nm).

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obtained from the absorption spectrum of FTC in the film state (Fig. 2). The energy band gaps obtained by the optical method and cyclic voltammetry were 2.55 eV and 3 eV, respectively. The electrochemically-estimated band gap  $(E_g^{el})$ , calculated using  $E_{g}^{el} = |LUMO - HOMO|$ , is slightly different from the optical band gap  $(E_g^{opt})$  obtained from the onset absorption. The electrochemical band gap  $(E_g^{el})$  is the energy difference between the LUMO and HOMO levels, which are in turn 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 estimating bases. Due to the fact that FTC is comprised of a conjugated fluorene core and three crown ethers, oxidation may start from the electron-donating crown ether parts, and reduction may start from the conjugated core of FTC.

# Electroluminescence enhancement of PLEDs by insertion of FTC

According to the energy band diagrams depicted in Fig. 3, the energy barrier between aluminum (Al) and PF-Green-B (2.16 eV) is larger than that between PEDOT:PSS and PF-Green-B (0.48 eV). Moreover, holes are usually more readily transported than electrons in conjugated materials, leading to a reduced recombination ratio of holes and electrons. Similar nonmatching energy barriers for electrons and holes are also apparent for the HY-PPV based device (Fig. 3). However, the charge injection/transport imbalance in PF-Green-B or HY-PPV can be alleviated by inserting the electron injection and hole blocking layer of FTC, in which both LUMO and HOMO energy levels are lower than those of PF-Green-B or HY-PPV. The lower LUMO and HOMO levels give rise to enhanced electron injection/transport and hole blocking, respectively, in PF-Green-B or HY-PPV based devices, resulting in more balanced charge recombination.

Multi-layer polymer light-emitting diodes (PLEDs) with a configuration of ITO/PEDOT:PSS/EML (PF-Green-B or HY-PPV)/ EIL/Al (80 nm) were fabricated to investigate their electroluminescence characteristics. In this work, we propose the use of water/alcohol-soluble **FTC** blended with  $M_2CO_3$  (M = Na, K, Cs)



Fig. 3 The energy band diagrams of PF-Green-B and HY-PPV, with those of FTC, PEDOT:PSS. and the electrodes.

or CH<sub>3</sub>COOM (M = Na, K) as an EIL in a PLED with PF-Green-B or HY-PPV as the EML. The optimal conditions for processing the EIL materials for use in PLEDs was to use water and alcohol (v/v = 1 : 5) as the solvent for spin-coating. The ratio of **FTC** : M<sup>+</sup> was fixed at 1 : 9 (azacrown : M<sup>+</sup> = 1 : 3), and the concentration was 1 mg **FTC** per ml. Current density–luminance–voltage (*J*–*L*–*V*) and luminous efficiency–power efficiency–current density (LE–PE–*J*) characteristics of the devices are shown in Fig. 4 and 5 and Fig. S6 and S7 (ESI<sup>†</sup>), with the corresponding optoelectronic data summarized in Tables 2 and 3. The electroluminescence performance was significantly enhanced by inserting the electron injection layer between the emitting layer (PF-Green-B or HY-PPV) and the Al cathode.

Maximum luminance and current efficiency of the devices were greatly increased from 1220 cd m<sup>-2</sup> and 0.72 cd A<sup>-1</sup> to 2920 cd m<sup>-2</sup> and 5.56 cd A<sup>-1</sup>, respectively, by inserting an electron injection layer (EIL: neat **FTC**) between the emitting layer (PF-Green-B) and the Al cathode [Fig. 4(a) and 5(a)]. Similar trends in the enhancement of device performance were also observed for the devices using HY-PPV as the emitting layer and neat **FTC** as the EIL [Fig. 4(b) and 5(b)]. The performance enhancement is attributable to the hole blocking and electron injection effect of **FTC**, which raises the charges recombination ratio. The lower HOMO level of **FTC** (-5.88 eV) than that of the emitting layer PF-Green-B (-4.52 eV) or HY-PPV (-5.0 eV)



**Fig. 4** Luminance *versus* voltage and current density *versus* voltage characteristics of PLEDs. Device structure: ITO/PEDOT:PSS/(a) PF-Green-B or (b) HY-PPV/EIL/AI.



Fig. 5 Current efficiency *versus* current density characteristics of PLEDs. Device structure: ITO/PEDOT:PSS/(a) PF-Green-B or (b) HY-PPV/EIL/AI.

results in the accumulation of holes at the interface between the emitting and **FTC** layers. Moreover, the lower LUMO level of **FTC** (-2.88 eV) than that of the emitting layer PF-Green-B (-2.14 eV) or HY-PPV (-2.8 eV) promotes electron injection (Fig. 3). Therefore, holes will readily combine with electrons passing through the interface to increase the recombination ratio.

The device performances using PF-Green-B or HY-PPV as the emitting layer were significantly enhanced in the presence of metal carbonates  $M_2CO_3$  (M = Na, K, Cs) (Tables 2 and 3). The devices using K<sub>2</sub>CO<sub>3</sub>-doped FTC as the EIL showed the best performance, *i.e.*, the maximum current efficiency and power efficiency of the device based on PF-Green-B (or HY-PPV) were further promoted to 21.58 cd  $A^{-1}$  and 12.42 lm  $W^{-1}$  (or 6.93 cd  $A^{-1}$  and 5.27 lm  $W^{-1}$ ), respectively (Fig. S6 and S7 in the ESI<sup>†</sup>). Moreover, these efficiencies are superior to those obtained with a conventional LiF/Al cathode (14.25 cd  $A^{-1}$  and 10.11 lm  $W^{-1}$ for PF-Green-B or 5.70 cd  $A^{-1}$  and 2.38 lm  $W^{-1}$  for HY-PPV) (Fig. S8 and S9 in the ESI<sup>†</sup>, Table 3). In addition, the turn-on voltages of the devices based on PF-Green-B or HY-PPV were decreased to 3.7 V or 2.5 V, which are much lower than the values of 5.7 V or 5.5 V obtained for the devices without FTC as the EIL, respectively (Tables 2 and 3). The electroluminescence enhancement is attributed to the effective promotion of electron injection/transport by the metal carbonate-doped FTC as the EIL, which leads to a higher charge recombination ratio.

To investigate the effects of the different counter anions  $(CO_3^- \text{ and } CH_3COO^-)$  on the electron injection ability, devices based on PF-Green-B or HY-PPV using metal acetate [CH3COOM (M = Na, K)-doped FTC as the EIL were also fabricated and their electroluminescence characteristics were investigated (Fig. 4 and 5). The device performances were also effectively enhanced in the presence of metal acetates  $CH_3COOM$  (M = Na, K) (Tables 2 and 3). The devices using CH<sub>3</sub>COOK-doped FTC as the EIL exhibit better performance than those using CH3COONa-doped FTC as the EIL. However, the metal carbonate-doped devices ( $M_2CO_3$ , M = Na, K) showed the best performance due to their higher dissociation rate than metal acetates (CH<sub>3</sub>COOM, M = Na, K). For instance, potassium carbonate dissociates more readily than potassium acetate, resulting in more abundant azacrown-chelated K<sup>+</sup>. The chelated K<sup>+</sup> can further reduce the electron injection barrier through the formation of an interfacial dipole and the establishment of an intermediate step for electron injection.26 Therefore, the potassium carbonate-doped FTC as the EIL effectively promoted electron injection/transport to significantly enhance the device performance.

To clarify the hole blocking effect of the EIL (neat FTC and doped FTC), hole-only devices [ITO/PEDOT:PSS/EML

Table 2         Optoelectronic properties of the light-emitting diodes based on PF-Green-B <sup>a</sup>								
EIL	$V_{\mathrm{on}}{}^{b}\left(\mathrm{V}\right)$	$L_{\max}^{c}$ (cd m <sup>-2</sup> )	$\operatorname{CE}_{\max}^{d} (\operatorname{cd} \operatorname{A}^{-1})$	$LPE_{max}^{e} (lm W^{-1})$	CIE $(x, y)^f$			
None	5.7	1220	0.72	0.27	(0.35, 0.62)			
LiF	3.6	14 390	14.25	10.11	(0.35, 0.62)			
FTC	5.7	2920	5.56	2.87	(0.36, 0.60)			
<b>FTC</b> + $Na_2CO_3$	3.7	13 770	15.77	9.23	(0.36, 0.61)			
<b>FTC</b> + $K_2CO_3$	3.7	17 460	21.58	12.42	(0.36, 0.61)			
<b>FTC</b> + $Cs_2CO_3$	4.0	17 380	16.26	9.96	(0.35, 0.62)			
FTC + CH <sub>3</sub> COONa	3.0	22 580	14.90	11.55	(0.38, 0.58)			
<b>FTC</b> + $CH_3COOK$	3.5	15 720	15.23	9.37	(0.38, 0.59)			

<sup>*a*</sup> [ITO/PEDOT:PSS/PF-Green-B (~100 nm)/EIL/Al (80 nm)]. <sup>*b*</sup> Turn-on voltage at 10 cd m<sup>-2</sup>. <sup>*c*</sup> Maximum luminance. <sup>*d*</sup> Maximum current efficiency. <sup>*e*</sup> Maximum luminous power efficiency. <sup>*f*</sup> The 1931 CIE coordinate at maximum luminance.

 Table 3
 Optoelectronic properties of the light-emitting diodes based on HY-PPV<sup>a</sup>

Paper

EIL	$V_{\mathrm{on}}^{b}(\mathrm{V})$	$L_{\max}^{c}$ (cd m <sup>-2</sup> )	$\operatorname{CE}_{\max}^{d} (\operatorname{cd} \operatorname{A}^{-1})$	$LPE_{max}^{e}$ (lm W <sup>-1</sup> )	$\operatorname{CIE}^{f}(x, y)$
None	5.5	680	0.07	0.03	(0.36, 0.61)
LiF	3.5	16 240	5.70	2.38	(0.41, 0.57)
FTC	3.1	3170	1.18	0.72	(0.40, 0.58)
<b>FTC</b> + $Na_2CO_3$	3.1	8220	2.88	1.34	(0.39, 0.59)
$FTC + K_2CO_3$	2.5	10 990	6.93	5.27	(0.41, 0.58)
$FTC + Cs_2CO_3$	2.8	13 340	4.61	3.02	(0.40, 0.58)
<b>FTC</b> + $CH_3COONa$	3.3	7150	2.34	1.12	(0.39, 0.59)
<b>FTC</b> + $CH_3COOK$	3.0	9980	3.09	1.49	(0.40, 0.58)
a =		h h h	- 2		

<sup>*a*</sup> [ITO/PEDOT:PSS/HY-PPV (~80 nm)/EIL/Al (80 nm)]. <sup>*b*</sup> Turn-on voltage at 10 cd m<sup>-2</sup>. <sup>*c*</sup> Maximum luminance. <sup>*d*</sup> Maximum current efficiency. <sup>*e*</sup> Maximum luminous power efficiency. <sup>*f*</sup> The 1931 CIE coordinate at Maximum luminance.

(PF-Green-B or HY-PPV)/EIL/Au (100 nm)] were fabricated to investigate their current density *versus* bias characteristics. As shown in Fig. 6, the curve shifts horizontally to higher bias after the insertion of **FTC** as the EIL, indicating the diminished current density under the same bias. However, the curve shifts slightly to a lower bias in the presence of metal carbonates or metal acetates, indicating that the hole blocking effect is diminished by the metal salts. However, the voltage-induced current densities are still lower than that of the device without an EIL. Therefore, more balanced charge injection and transport was achieved by inserting the metal carbonate- or metal acetate-doped **FTC** layer, which promoted electron injection and adjusts hole blocking simultaneously.

To demonstrate the electron injection ability of the EIL (neat FTC and doped FTC), electron-only devices [glass/PEDOT:PSS/Ag (100 nm)/EML (PF-Green-B or HY-PPV)/EIL/A1 (80 nm)]<sup>34,35</sup>



**Fig. 6** Current density *versus* voltage characteristics of hole-only PLEDs. Device structure: ITO/PEDOT:PSS/(a) PF-Green-B or (b) HY-PPV/EIL/Au.

Fig. 7 Current density versus voltage characteristics of electron-only PLEDs. Device structure: ITO/PEDOT:PSS/Ag/(a) PF-Green-B or (b) HY-PPV/EIL/AI.

were fabricated to investigate their current density *versus* bias characteristics (Fig. 7). The current density (under the same bias) is increased by the EILs, especially in the device using  $K_2CO_3$ -doped **FTC** as the EIL, which shows the highest current density. This is attributed to the enhancement in electron injection/transport by the EILs. Moreover, for the devices with  $K_2CO_3$ -doped **FTC** as the EIL, the current densities of the hole-only and electron-only devices are the closest, compared to those with neat **FTC** or without EIL (Fig. 8). This suggests that the  $K_2CO_3$ -doped **FTC** is the most effective EIL to balance charge injection and transport.

Photovoltaic (PV) measurements were conducted to demonstrate that the addition of metal carbonates and metal acetates plays a crucial role in promoting electron injection in the PLEDs. When the anode is kept the same (ITO/PEDOT:PSS), the open-circuit voltage ( $V_{oc}$ ) is primarily determined by the effective work-function of the cathode, which reflects the electron-injection ability of the EIL materials.<sup>11,36</sup> The  $V_{oc}$  values were 0.36 V and 0.96 V for the devices based on PF-Green-B and HY-PPV without EIL, respectively, which increased to 1.28 V and 1.16 V when neat **FTC** was inserted as the EIL (Fig. 9). They were further raised to 1.74 V and 1.62 V when K<sub>2</sub>CO<sub>3</sub>-doped **FTC** was



Fig. 8 Current density versus voltage characteristics of electron-only and holeonly PLEDs.

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**Fig. 9** Photovoltaic measurements of PLEDs using **FTC** and doped-**FTC** as the electron injection layer. Device structure: ITO/PEDOT:PSS/PF-Green-B or HY-PPV/ EIL/AI.

used as the EIL. A higher  $V_{oc}$  means that the built-in potential (the difference in work function between the anode and the cathode) across the anode/EML/cathode junction has been increased. Moreover, the highest  $V_{oc}$  values (1.74 V and 1.62 V) correspond to the best device performances for the devices using K<sub>2</sub>CO<sub>3</sub>-doped **FTC**. Therefore, a drop in the work function of the EIL/Al cathode (or a generation of interfacial dipoles at the EIL/metal junction) has been realized by inserting the EIL. A lower work function of the cathode usually facilitates electron injection. Accordingly, the significant performance enhancement in the devices using doped **FTC** as an EIL should mainly be attributed to the enhanced electron injection ability. Current results indicate that the fluorene-cored **FTC** with azacrown ether groups is a promising stable cathode modifier for promoting electron injection and device performance.

### Conclusion

We have presented a novel water/alcohol-soluble fluorene-cored **FTC** with triple-azacrown ether groups as an electron injection layer (EIL) for the fabrication of multilayer PLEDs by a spin-coating process. The **FTC** is a highly efficient EIL, especially

after the addition of metal carbonates  $M_2CO_3$  (M = Na, K, Cs) and metal acetates  $CH_3COOM$  (M = Na, K). We also investigated the effect of different counter anions (CO<sub>3</sub><sup>-</sup> and CH<sub>3</sub>COO<sup>-</sup>) on the electron injection ability of the devices based on PF-Green-B or HY-PPV. The metal carbonate-doped devices showed the best performance due to their higher dissociation rate than metal acetates. The devices based on PF-Green-B or HY-PPV as the emission layer with K<sub>2</sub>CO<sub>3</sub>-doped FTC as the EIL (ITO/PEDOT:PSS/PF-Green-B or HY-PPV/EIL/Al) revealed the best device performance. For the devices based on PF-Green-B (and HY-PPV), their maximum current efficiency and maximum luminous power efficiency were 21.58 cd  $A^{-1}$  (6.93 cd  $A^{-1}$ ), and 12.42 lm  $W^{-1}$  (5.27 lm  $W^{-1}$ ), respectively, which were superior to those of the device without an electron injection layer. In addition, the turn-on voltages were also significantly reduced (from 5.7 V to 3.0 V for PF-Green-B, and from 5.5 V to 2.5 V for HY-PPV). The electron- and holeonly devices and their open circuit voltages  $(V_{oc})$  were investigated to clarify their charge injection/transport abilities. The performance enhancement has been attributed to hole blocking and promoted electron injection/transport by the inserted EIL. The present results demonstrate that FTC doped with metal carbonates and metal acetates is an effective electron injection/transport material, applicable for use in optoelectronic devices.

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### Notes and references

- 1 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackey, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, 347, 539.
- 2 J. R. Sheats, H. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. B. Roitman and A. Stocking, *Science*, 1996, **273**, 884.
- 3 R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, D. D. C. Bradley, D. A. D. Santos, J. L. Bredas, M. Loglund and W. R. Salaneck, *Nature*, 1999, 397, 121.
- 4 Organic Light-Emitting Devices: Synthesis, Properties and Applications, ed. K. Mullen and U. Scherf, Wiley-VCH, Weinheim, 2006.
- 5 Y. Z. Lee, X. Chen, S. A. Chen, P. K. Wei and W. S. Fann, *J. Am. Chem. Soc.*, 2001, **123**, 2296.
- 6 F. Garten, A. Hilberer, F. Cacialli, E. Esselink, Y. V. Dam,
  B. Schlatmann, R. H. Friend, T. M. Klapwijk and
  G. Hadziioannou, *Adv. Mater.*, 1997, 9, 127.
- 7 J. S. Kim, R. H. Friend and F. Cacialli, *Appl. Phys. Lett.*, 1999, 74, 3084.
- 8 Q. Huang, G. Evmenenko, P. Dutta, P. Lee, N. R. Armstrong and T. J. Marks, *J. Am. Chem. Soc.*, 2005, **127**, 10227.
- 9 S. Kato, J. Am. Chem. Soc., 2005, 127, 11538.
- 10 D. Braun and A. J. Heeger, Appl. Phys. Lett., 1991, 58, 1982.

- 11 H. Wu, F. Huang, Y. Mo, W. Yang, D. Wang, J. Peng and Y. Cao, *Adv. Mater.*, 2004, **16**, 1826.
- 12 T.-W. Lee, H.-C. Lee and O. O. Park, *Appl. Phys. Lett.*, 2002, **81**, 214.
- 13 T. F. Guo, F. S. Yang, Z. J. Tsai, T. C. Wen, S. N. Hsieh and Y. S. Fu, *Appl. Phys. Lett.*, 2005, 87, 13504.
- 14 X. Y. Deng, W. M. Lau, K. Y. Wong, K. H. Low, H. F. Chow and Y. Cao, *Appl. Phys. Lett.*, 2004, **84**, 3522.
- 15 S. H. Jin, M. Y. Kim, J. Y. Kim, K. Lee and Y. S. Gal, *J. Am. Chem. Soc.*, 2004, **126**, 2474.
- 16 F. Huang, H. B. Wu, D. L. Wang, W. Yang and Y. Cao, *Chem. Mater.*, 2004, 16, 708.
- 17 F. Huang, Y. H. Niu, Y. Zhang, J. W. Ka, M. S. Liu and A. K. Y. Jen, *Adv. Mater.*, 2007, **19**, 2010.
- 18 F. Huang, Y. Zhang, M. S. Liu and A. K. Y. Jen, Adv. Funct. Mater., 2009, 19, 2457.
- 19 S. H. Oh, D. Vak, S. I. Na, T. W. Lee and D. Y. Kim, *Adv. Mater.*, 2008, **20**, 1624.
- 20 R. Yang, H. Wu, Y. Cao and G. C. Bazan, J. Am. Chem. Soc., 2006, **128**, 14422.
- 21 C. V. Hoven, A. Garcia, G. C. Bazan and T. Q. Nguyen, *Adv. Mater.*, 2008, **20**, 3793.
- 22 X. Xu, B. Han, J. Chen, J. Peng, H. Wu and Y. Cao, *Macromolecules*, 2011, 44, 4204.
- 23 F. Huang, P. I. Shih, C. F. Shu, Y. Chi and A. K.-Y. Jen, Adv. Mater., 2009, 21, 361.
- 24 C. J. Pedersen, J. Am. Chem. Soc., 1967, 89, 2495.
- 25 C. J. Pedersen, Angew. Chem., Int. Ed. Engl., 1988, 27, 1021.
- 26 H. H. Lu, Y. S. Ma, N. J. Yang, G. H. Lin, Y. C. Wu and S. A. Chen, *J. Am. Chem. Soc.*, 2011, 133, 9634.
- 27 (a) M. Kreyenschmidt, G. Klaerner, T. Fuhrer, J. Ashenhurst,
  S. Karg, W. D. Chen, V. Y. Lee, J. C. Scoot and R. D. Miller, *Macromolecules*, 1998, 31, 1099; (b) A. W. Grice,
  D. D. C. Bradley, M. T. Bernius, M. Inbasekaran, W. W. Wu
  and E. P. Woo, *Appl. Phys. Lett.*, 1998, 73, 629.
- 28 (a) U. Scherf and E. J. W. List, Adv. Mater., 2002, 14, 477; (b)
  S. Becker, C. Ego, A. C. Grimsdale, E. J. W. List, D. Marsitzky,
  A. Pogantsch, S. Setayesh, G. Leising and K. Müllen, Synth. Met., 2001, 125, 73; (c) A. Babel and S. A. Jenekhe, Macromolecules, 2003, 36, 7759; (d) N. S. Cho,
  D.-H. Hwang, B.-J. Jung, E. Lim, J. Lee and H.-K. Shim, Macromolecules, 2004, 37, 5265.
- (a) C.-S. Wu and Y. Chen, Macromolecules, 2009, 42, 3729; (b)
  C.-S. Wu and Y. Chen, J. Mater. Chem., 2010, 20, 7700; (c)
  C.-S. Wu and Y. Chen, J. Polym. Sci., Part A: Polym. Chem., 2010, 48, 5727; (d)
  C.-S. Wu, S.-L. Lee and Y. Chen, J. Polym. Sci., Part A: Polym. Chem., 2011, 49, 3099; (e)
  C.-S. Wu and Y. Chen, J. Polym. Chem., 2011, 49, 3099; (e)
  C.-S. Wu and Y. Chen, J. Polym. Sci., Part A: Polym. Chem., 2011, 49, 3928; (f)
  C.-S. Wu, Y.-J. Yang, S.-W. Fang and Y. Chen, J. Polym. Sci., Part A: Polym. Chem., 2012, 50, 3875; (g)
  C.-S. Wu, Y.-T. Lee and Y. Chen, Polym. Chem., 2012, 3, 2776; (h)
  C.-S. Wu, C.-T. Liu and Y. Chen, Polym. Chem., 2012, 3, 2012, 32, 23877; (j)
  C.-S. Wu, C.-P. Chen and Y. Chen, J. Polym. Sci., Part A: Polym. Chem., 2013, 51, 3975; (k)
  C.-S. Wu, S.-W. Fang and Y. Chen, Phys. Chem. Chem. Phys., 2013, 15, 15121.

- 30 T. Bernius, M. Inbasekaran, J. O'Brien and W. Wu, *Adv. Mater.*, 2000, **12**, 1737.
- 31 M. W. Lin, C. T. Wen, Y. J. Hsu and T. F. Guo, *J. Mater. Chem.*, 2011, **21**, 18840.
- 32 T. H. Lee, J. C. A. Huang, T. F. Guo, T. C. Wen, Y. S. Huang, C. C. Tsou, C. T. Chung, Y. C. Lin and Y. J. Hsu, *Adv. Funct. Mater.*, 2008, 18, 3036.
- 33 L. Scholer, K. Seibel, K. Panczyk and M. Bohm, *Microelectron. Eng.*, 2009, **86**, 1502.
- 34 K. Manabe, W. Hu, M. Matsumura and H. Naito, J. Appl. Phys., 2003, 94, 2024.
- 35 R. Steyrleuthner, S. Bange and D. Neher, J. Appl. Phys., 2009, 105, 064509.
- 36 L. S. Yu and S. A. Chen, Adv. Mater., 2004, 16, 744.