

Creating a Pseudometallic State of K^+ by Intercalation into 18-Crown-6 Grafted on Polyfluorene as Electron Injection Layer for High Performance PLEDs with Oxygen- and Moisture-Stable Al Cathode

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Supporting Information

ABSTRACT: Polymer light-emitting diodes (PLEDs) suffer from inadequate lifetimes because of the use of environmentally sensitive metals as the cathodes. We present the use of water/methanol-soluble polyfluorene grafted with 18-crown-6 chelating to K^+ as the electron-injection layer (EIL) for deep-blue-emission PLEDs, allowing the use of environmentally stable Al as the cathode since electron donation from the 18-crown-6 can reduce K^+ to a stable “pseudometallic state”, enabling it to act as an intermediate step for electron injection. Furthermore, when poly(ethylene oxide) was blended into the EIL to provide hole blocking (HB), 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^2 and an external quantum efficiency of 5.42%. The use of such an EI–HB layer opens a broad avenue leading toward industrialization of PLEDs.

The development of polymer light-emitting diodes (PLEDs) with practically acceptable lifetimes is an important issue for realization of their industrialization. Therefore, 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 because the formation of interfacial dipole or space charge between the emitting layer (EML) and the cathode can reduce the electron-injection barrier.^{1–7} Consequently, the maximum external quantum efficiencies η_{ext} (and the corresponding maximum luminous efficiencies η_L) for blue-, green-, and red-emission PLEDs using fluorescent conjugated polymers as the EMLs and Al as the cathode have been reported to reach 1.62% (1.3 cd/A),² 7.85% (23.8 cd/A),² and 2.94% (2.89 cd/A),⁴ respectively. However, the brightnesses (at the applied voltage) at the η_{ext} for the three emissions are only 380 cd/m^2 (9.7 V), 7923 cd/m^2 (8.8 V), and 1040 cd/m^2 (9.4 V), respectively, which are far lower than the deep-blue-emission brightness of 54 800 cd/m^2 (6.6 V) at 5.42% (6.14 cd/A) obtained in the present work, as revealed below.

In addition to the above hydrophilic groups,^{1–7} crown ether groups may be expected to serve the same purpose. Polyfluorene grafted with 15-crown-4 moieties (PFC) was used as an EIL for a

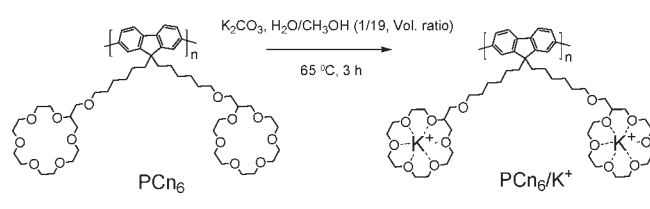
poly(9,9-dihexylfluorene)-based device with Ca as the cathode to reduce the turn-on voltage V_{on} from 6.6 V (without PFC) to 4.1 V (with PFC) and enhance the maximum brightness B_{max} (and η_L) from 880 cd/m^2 (0.29 cd/A) to 2800 cd/m^2 (0.53 cd/A); this was attributed to the formation of an interfacial dipole.⁸ Crown ethers are a special class of ether able to form stable complexes with alkali, alkaline-earth, and transition-metal ions.^{9,10} A metal ion with diameter close to the cavity diameter of a crown ether can form a stable complex with it.¹⁰ For example, the cavities of 12-crown-4 (1.2–1.5 Å), 15-crown-5 (1.7–2.2 Å), and 18-crown-6 (2.6–3.2 Å) can form stable complexes with Li^+ (1.36 Å), Na^+ (1.94 Å), and K^+ (2.66 Å), respectively.¹⁰

Here we propose the use of a water- or alcohol-soluble 18-crown-6 (Cn6)-grafted polyfluorene (PCn6; see Chart S1 in the Supporting Information) blended with K_2CO_3 as the EIL in a PLED with β -phase-containing poly(9,9-di-*n*-octylfluorene) (β -PFO) as the EML. β -PFO, which exhibits a deep-blue emission with high spectral stability in electroluminescence (EL),¹¹ here was formed by spin-coating of ethyl acetate on top of an amorphous PFO film. [It should be noted that the photoluminescence quantum efficiency (PLQE) of β -PFO is 62%, which is higher than that of amorphous PFO (39%)]. The solubility in highly polar solvents (e.g., water or alcohol) provided by Cn6 can prevent dissolution of the EML having a thin EIL atop it, and the intercalation of K^+ into Cn6 (Scheme 1) allows the K^+ ion to act similarly to potassium metal (and here is termed a “pseudometallic state”) in reducing the electron-injection barrier from a stable metal cathode (e.g., Al or Au) and facilitating electron transport. Furthermore, blending poly(ethylene oxide) (PEO) into the K_2CO_3 -blended PCn6 layer (at a Cn6: K^+ mole ratio of 1:3) to provide hole-blocking (HB) functionality can remarkably enhance the device performance, affording the highest performance reported to date for a deep-blue PLED with a conjugated polymer as the EML. Chemical structures of 15-crown-5 (Cn5)-grafted polyfluorene (PCn5), PEO, and PFO are shown in Chart S1.

We first define the notation for the EI–HB layers used in this study. The label PCn6: $K^+(1:x)$ indicates that the layer is composed of PCn6 and K_2CO_3 , and 1: x in the parentheses ($x = 0, 1, 3$) is the Cn6: K^+ mole ratio. PCn6:PEO(1: y) indicates that the layer is composed of PCn6, K_2CO_3 , and PEO with a Cn6: K^+ mole ratio of 1:3, and 1: y in parentheses ($y = 0.75, 1, 1.5, 2$) is the PCn6:PEO mass ratio. Finally, PCn6: $K^+(1:x)/Al$ [or PCn6:PEO(1: y)/Al] and PCn6: $K^+(1:x)/Au$ [or PCn6:PEO(1: y)/Au] denote β -PFO-based devices with Al and Au,

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Scheme 1. Chelation of Cn6 to K^+ Table 1. Characteristic PLED Performance Values for β -PFO-Based Devices without and with EI-HB Layers^a

	V_{on} (V) ^b	B_{max} (cd/m ²)	η_L (cd/A)
without EI-HB layer	10	12	0.017
PCn6:K ⁺ (1:0)	5.8	624	0.17
PCn6:K ⁺ (1:1)	3.6	18300	1.88
PCn6:K ⁺ (1:3)	3.6	26500	2.03
PCn6:PEO (1:0.75)	3.4	54800	6.14
PCn6:PEO (1:1)	3.8	47100	5.95
PCn6:PEO (1:1.5)	3.4	38800	5.45
PCn6:PEO (1:2)	3.8	8900	1.65

^aThe device structure was ITO/PEDOT (25 nm)/ β -PFO (120 nm)/[without/with EI-HB layer (20 nm)]/Al (60 nm). ITO and PEDOT are abbreviations for indium tin oxide and poly(styrene sulfonic acid)-doped poly(3,4-ethylenedioxythiophene), respectively.

^bBrightness at 2 cd/m².

respectively, as the cathode. This notation system has also been applied to the case of PCn5 blended with K_2CO_3 and to the cases of PCn6 and PCn5 blended with Li_2CO_3 , Na_2CO_3 , and CS_2CO_3 with a crown ether:metal ion mole ratio of 1:1. In addition, PEO:K⁺ (6:3) indicates that the layer contains PEO and K_2CO_3 at a PEO (repeat unit):K⁺ mole ratio of 6:3.

Table 1 shows the characteristic PLED performance of β -PFO-based devices without and with EI-HB layers, and their characteristic curves of current density (J) and brightness (B) versus voltage and of luminous efficiency versus J are shown in Figure 1. The J profile of PCn6:K⁺ (1:0)/Al obviously increased in comparison with that of the device without this layer (Figure 1A). When K_2CO_3 was blended into PCn6 with a Cn6:K⁺ mole ratio of 1:1 or 1:3, the corresponding device exhibited remarkably a higher J profile than PCn6:K⁺ (1:0)/Al. For example, J of PCn6:K⁺ (1:3)/Al at 6 V was larger than those of PCn6:K⁺ (1:1)/Al, PCn6:K⁺ (1:0)/Al, and the device without an EI-HB layer by factors of 1.2, 74, and 1700, respectively. Similarly, the B profiles followed the same trend (Figure 1B), and PCn6:K⁺ (1:3)/Al gave $B_{max} = 26\,500$ cd/m², which is dramatically higher than that from the device without an EI-HB layer (12 cd/m²). In addition, V_{on} decreased dramatically, from 10 V (no EI-HB layer) to 5.8 V [PCn6:K⁺ (1:0)/Al] to 3.6 V [PCn6:K⁺ (1:1 or 1:3)/Al]. Also, PCn6:K⁺ (1: x)/Al exhibited a much higher η_L than the device without this layer, reaching the highest value (2.03 cd/A) at the Cn6:K⁺ mole ratio of 1:3. Obviously, the device performance with Al as the cathode was remarkably enhanced when the water/methanol-soluble PCn6:K⁺ was inserted as the EIL. Because no change was made on the ITO/PEDOT anode, the enhanced device performance can be attributed to the increased electron current density resulting from the reduction of the electron-injection barrier provided by PCn6:K⁺ (1: x) layers through the formation of an interfacial dipole (Text S1 and Figure S1).

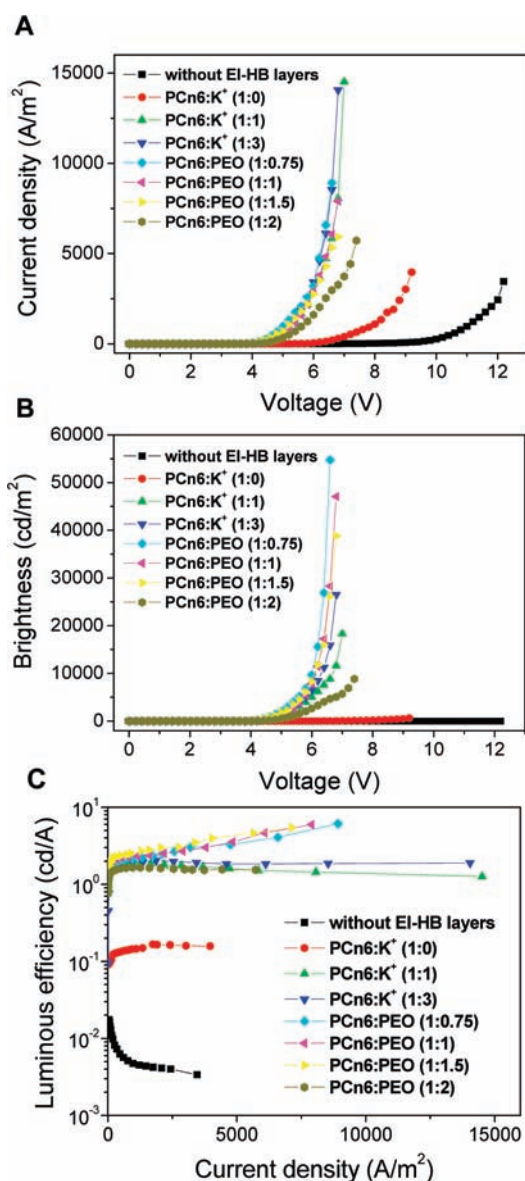


Figure 1. Characteristic PLED curves of (A) current density and (B) brightness vs voltage and (C) luminous efficiency vs current density for β -PFO-based devices without and with EI-HB layers. The device structure was ITO/PEDOT (25 nm)/ β -PFO (120 nm)/[without/with EI-HB layer (20 nm)]/Al (60 nm).

Since the open-circuit voltage (V_{oc}) of a device reflects the built-in potential (the difference in work function between anode and cathode) across its anode/EML/cathode junction, it can be used to investigate the change in the electron-injection barrier of devices due to the formation of an interfacial dipole with or without insertion of an additional layer between the EML and cathode.^{2,12} In order to demonstrate that the chelated K⁺ plays another role in barrier reduction, we plotted the reduced current density $J/J_{bare-Al}$ (where the subscript "bare-Al" refers to a device with only Al as the cathode and without an EI-HB layer) versus $V_{oc} - V_{oc,bare-Al}$ [V_{oc} values for PCn6:K⁺ (1: x)/Al and PCn5:K⁺ (1: x)/Al were taken from Figures S1 and S5, respectively]. As shown in Figure 2, $J/J_{bare-Al}$ dramatically increased from 23 with only PCn6 to 1411 with PCn6:K⁺ (1:1). However, the corresponding V_{oc} differences (relative to $V_{oc,bare-Al}$) increased only

from 0.83 to 1.01 V. Obviously, the added K^+ plays another role in barrier reduction in addition to the formation of an interfacial dipole because it causes an increase in $J/J_{\text{bare-Al}}$ larger than that expected from the increase in the V_{oc} difference. The additional function is attributed to the formation of a pseudometallic state of K^+ when K^+ is chelated by Cn6 [as revealed by X-ray photoelectron spectroscopy (XPS) data below] that provides an intermediate step beneficial for electron injection from the cathode to the EIL. The dramatic increase of $J/J_{\text{bare-Al}}$ also happens in the case of PCn5: $K^+(1:x)$ /Al but to a lesser extent, indicating that the inference of a pseudometallic state that enhances electron injection is reasonable. In addition, the $J/J_{\text{bare-Al}}$ of PCn6: $K^+(1:3)$ /Al (1700) is larger than those without K^+ intercalation calculated from the data in refs 2, 3, 5, and 6, indicating the extraordinary effect of the pseudometallic state on the enhancement of electron injection.

For further effective utilization of injected holes from the anode, PEO was incorporated into the EIL by blending to provide the HB function (Text S2). At a PCn6:PEO mass ratio of 1:0.75, the device performance of PCn6: $K^+(1:3)$ /Al with the color coordinates CIE_{xy} (0.160, 0.113) was further enhanced to $B_{\text{max}} = 54\,800\text{ cd/m}^2$ and $\eta_L = 6.14\text{ cd/A}$ ($\eta_{\text{ext}} = 5.42\%$), which are the highest values reported to date for deep-blue PLEDs with a conjugated polymer as the EML (Text S3 and Figure S2). Further increases in the PEO content led to a decrease in device performance. For PCn6:PEO-(1:2)/Al, B_{max} and η_L decreased to 8900 cd/m^2 and 1.65 cd/A , respectively, as a result of the fact that too many holes were blocked and fewer electrons were injected, as indicated by the lower current density than for PCn6: $K^+(1:3)$ /Al (e.g., by a factor of 2.1 at 6 V; Figure 1A). On the other hand, the EL spectra of the devices with EI-HB layers and that of the device based on the PCn6: $K^+(1:3)$ film as the EML were quite different, demonstrating that the EI-HB layer does not emit light and that the undesired green emission does not grow during operation for the devices with EI-HB layers (Text S4 and Figure S3). In addition, chelation of PCn6 and PCn5 to other metal ions with different sizes (Li^+ , Na^+ , and Cs^+) could also enhance device performance as in the cases of chelation to K^+ (Text S5 and Tables S1 and S2).

The evidence for the formation of the pseudometallic state is presented below. We performed XPS measurements on PCn6: $K^+(1:1)$ and $-(1:3)$ films to investigate the interaction between Cn6 and K^+ in the Cn6/ K^+ complex. As shown in Figure 3, the characteristic electron binding energies of K $2p_{3/2}$ and K $2p_{1/2}$ in K_2CO_3 are 294.11 and 296.91 eV, respectively. In the Cn6/ K^+ complex, these two binding energies shifted by 0.5 eV to the lower values 293.61 and 296.41 eV, respectively. This indicates that K^+ receives extra electrons from the oxygen atoms in Cn6, causing its electronic states (K $2p_{3/2}$ and K $2p_{1/2}$) to shift toward those of potassium metal (K $2p_{3/2}$, 292.60 eV; K $2p_{1/2}$, 295.50 eV).¹³ For the case of the dibenzo-18-crown-6/ K^+ complex, the two K 2p binding energies were found to be independent of the counterion (Cl^- , Br^- , or I^-), implying that electron donation from the lone-pair electrons of the oxygen atoms can effectively stabilize K^+ .¹⁴ This new state of K^+ is thus termed a “pseudometallic state” and is expected to provide a bridge for electron injection and transport between the high-work-function Al metal and the EML. In addition, from these XPS results, the fractions of Cn6 chelated to K^+ were determined by deconvolution of the K 2p signal peaks to be 39.5 and 94.7% for the mole ratios 1:1 and 1:3, respectively (Text S6 and Figure S4). The latter is higher than the former by a factor of 2.4, accounting for the larger observed V_{oc} value for

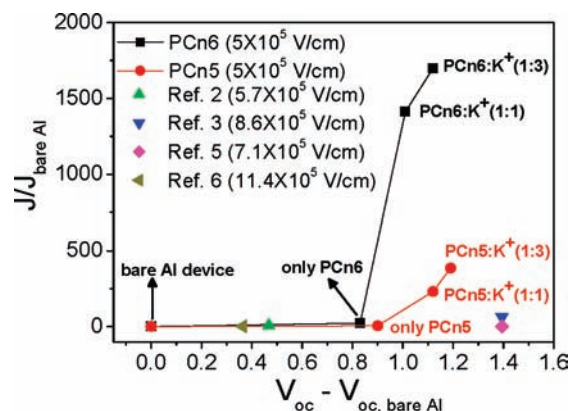


Figure 2. Reduced current density ($J/J_{\text{bare-Al}}$) vs $V_{\text{oc}} - V_{\text{oc,bare-Al}}$ for PCn6: $K^+(1:x)$, PCn5: $K^+(1:x)$, and literature data. Values in parentheses are the electric fields at which the J values were recorded.

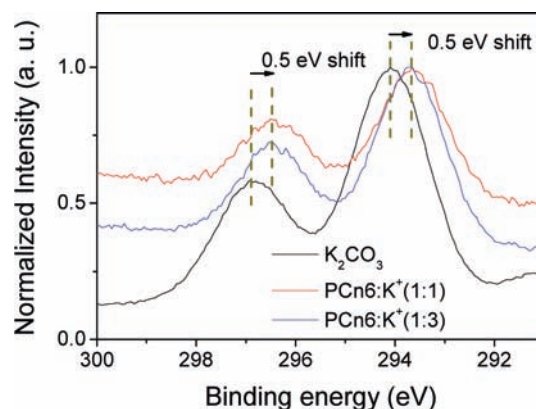


Figure 3. XPS spectra (K 2p) of K_2CO_3 , PCn6: $K^+(1:1)$, and PCn6: $K^+(1:3)$ films.

Cn6: $K^+(1:3)$ /Al (2.36 V, Figure S1) than for Cn6: $K^+(1:1)$ /Al (2.25 V, Figure S1).

However, the lowering of the electron-injection barrier by the EILs cannot completely explain the difference in performance between devices with Cn6/ K^+ and Cn5/ K^+ (Text S7 and Figures S5 and S6). We found that facilitating electron transport in these EILs is also important for increasing the electron current density,¹⁵ and the stronger interaction between K^+ and Cn6 can form more K^+ channels across the EIL for electron transport (Text S7 and Figures S7 and S8). Figure 4 illustrates the K $2p_{3/2}$ binding energies of various K/K^+ states, and one can see that the interaction between Cn6 and K^+ is stronger than the Cn5/ K^+ and PEO/ K^+ interactions because its binding energy is closer to that of potassium metal than the others (Text S8 and Figure S9). Therefore, we propose the working mechanism of the EI-HB layer as illustrated in Figure 5. The chelated K^+ can further reduce the electron-injection barrier through the formation of an interfacial dipole [e.g., the barrier was reduced by 1.12 eV for insertion of the PCn6: $K^+(1:3)$ layer relative to the value without the layer] and the establishment of an intermediate step for electron injection. Therefore, electrons can be directly injected into the backbone of PCn6 or chelated K^+ . Because the lowest unoccupied molecular orbital (LUMO) of PCn6 should be closer to the vacuum level than the energy level of chelated K^+ , one can expect that the electrons originally injected into the backbone of

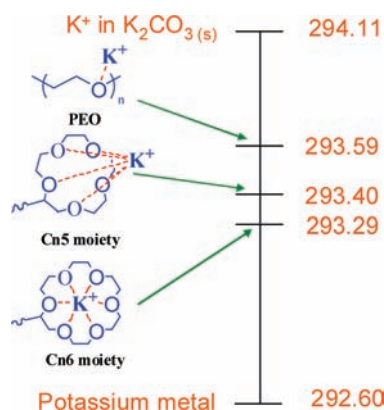


Figure 4. K $2p_{3/2}$ binding energies (in eV) of various K/K⁺ states.

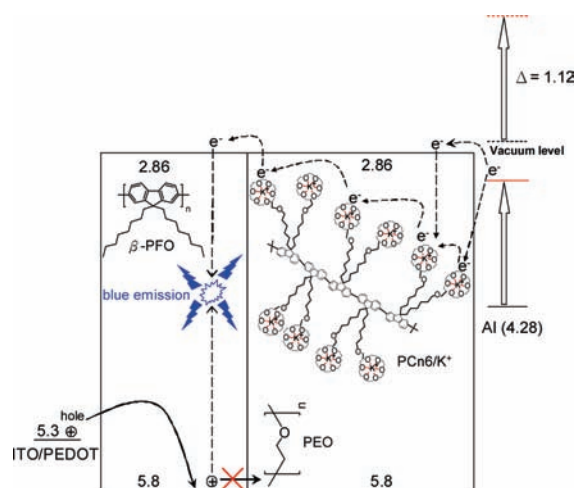


Figure 5. Schematic illustration of the working mechanism proposed in this study. The numbers are energy levels in eV taken from the literature.^{11,16} Δ denotes the shift of the vacuum level.

PCn6 will spontaneously hop to the chelated K⁺. The chelated K⁺ can form electron-transport channels through which the electrons can migrate to the EIL–EML interface. The electrons can then easily hop to the EML because the chelated K⁺ is in the pseudometallic state resembling potassium metal. In short, the existence of chelated K⁺ can facilitate electron injection from the Al cathode (work function = 4.28 eV)¹⁶ to the EML (its LUMO level is 2.86 eV).¹¹ In addition, PEO provides HB functionality to increase the hole–electron recombination fraction in the EML and therefore enhance the device performance. This proposed mechanism is further supported by the fact that including the EI–HB layer was useful when Au was used as the cathode (Text S9 and Table S3).

Notably, this mechanism for the enhancement of device performance is different from that in polymer light-emitting electrochemical cells (PLECs), in which the generation of n- and p-doped conjugated polymer layers at two electrode interfaces by addition of an ionic salt under an electric field is involved.^{17,18} In the present case, the η_L values for devices with Au as the cathode were lower than those with Al as the cathode by a factor of 30–70 (Text S9 and Table S3), indicating that the device performance based on the EI–HB layers strongly depends on the cathode material used. For LECs, the device performance was independent of the electrode material used.

In summary, we have presented the use of water/methanol-soluble polyfluorene grafted with Cn6 chelated to K⁺ as an EIL

for deep-blue-emission PLEDs, which allows the use of environmentally stable Al as the cathode because electron donation from the crown ether (Cn6) can reduce K⁺ to a stable “pseudometallic state”. Furthermore, when PEO was blended into the EIL (at a Cn6:K⁺ mole ratio of 1:3) to provide a hole-blocking effect, the device exhibited the highest performance reported to date for deep-blue emission, $B_{\max} = 54\,800$ cd/m² and $\eta_{\text{ext}} (\eta_L) = 5.42\%$ (6.14 cd/A), which are much higher even than those obtained using CsF/Al as the cathode (34 326 cd/m², 3.33%, and 3.85 cd/A). The introduction of a stable pseudometallic state as an intermediate step for effective electron injection and transport opens a broad avenue leading toward industrialization of PLEDs.

■ ASSOCIATED CONTENT

S Supporting Information. Description of experimental data, syntheses of monomers and polymers, chelation, device fabrication and instrumentation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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