Concomitant tuning of metal work function and wetting property with mixed self-assembled monolayers

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ABSTRACT

The effect of the surface composition of a mixed self-assembled monolayer on the work function and wetting property of silver substrate are investigated with the mixtures of a fluorinated alkanethiol and a carboxyl-terminated alkanethiol of various chain lengths. The work function of silver can be tuned from 4.3 to 5.3 eV by changing the mixing ratio while the wetting property can be modulated by adjust the relative chain length of the fluorinated thiol and the carboxyl-terminated thiol. Thus solution-processed poly(para phenylene vinylene)-based polymer light-emitting diode was made possible with high efficiency of 6.7 cd/A and brightness of 40,000 cd/m^2.

1. Introduction

The operation of most organic semiconductor devices depends on a proper energy alignment of the metal electrodes and the organic layers. For example, low energy barriers for both hole and electron injection are required for the organic light-emitting diode, whereas the organic transistor requires Ohmic contact between the source-drain and the semiconductor [1–3]. For relatively stable and common metals, there are however practically very few choices of work functions: 4.3 eV for silver and aluminum, and 5.0 eV for gold [4–6]. The device design will become much more flexible if the work functions of the metals can be continuously tuned in a wide range. Modification/ treatment of a metal surface by the adsorption of a specific species changes the tendency for charge departure from or attraction to the surface due to the local dipole moment introduced by the adsorbates [7–9]. In particular,

self-assembled monolayers (SAMs) have been used to systematically modulate the work function of a metal through the various functional groups of the adsorbed molecules. Among these, SAMs of fluorinated hydrocarbon chains have been frequently used to increase the work function of various electrodes due to the strongly electron-withdrawing fluorine atoms [10–12]. It is demonstrated that carrier injection in hole-only devices can be enhanced by such modification. Whereas, SAMs of hydrocarbon were found to decrease the work function and suppress hole charge injection [13]. It is further demonstrated that continuous tuning of the work function can be achieved by the use of mixed SAMs of a fluorocarbon and a hydrocarbon [13,14], so that the amount of hole carriers can be systematically modulated by controlling the composition of the two compounds [13]. However, for devices prepared by solution process such as spin coating, there is a dilemma that the highly electronegative fluorine atoms provide not only the desired dipole moment for work function tuning but also the undesired poor wettability due to the low surface energy of the substrate it creates. In a mixed SAM where fluorinated hydrocarbon is mixed with a non-polar

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hydrocarbon component, wettability did not improve because the non-polar nature of hydrocarbon component, but the work function is reduced simultaneously. The poor wettability may cause problem in process such as spin-coating as the semiconducting materials may not adhere to the substrate. It is therefore of interest to control the work function and the wetting property of the metal independently.

Mixed monolayers containing one hydrophobic component and one hydrophilic component offer the opportunity to modulate the wetting property of the surface over a wide range [15]. It has also been demonstrated that the contact angle is highly surface-sensitive since the wetting liquid senses the structural change at the very top 2–3 Å region of the surface [15]. Thus by controlling the relative chain length of the two components, it is possible to "shield" the non-wetting character of one component by the wetting character of the other, or vice versa. In this work, mixtures of a fluorinated alkanethiol and a carboxyl-terminated alkanethiol with different chain lengths are used to form mixed SAMs on silver substrate in order to decouple their effect on the work function and surface wetting. The fluorinated alkanethiol serves to increase the work function, whereas the carboxyl-terminated alkanethiol is used to impart the needed wettability. The effect of the carboxyl group can be further enhanced by adjusting the relative chain length of the two in the mixture. As shown in Fig. 1(b), the carboxyl-terminated thiol is chosen to be longer than the fluorinated thiol such that solution containing the semiconductor is in contact mostly with the hydrophilic carboxyl groups. In the case where the two components are of the same chain length (Fig. 1(a)), the solution is in contact with both the hydrophilic carboxyl groups and the hydrophobic CF_3 groups. By forming mixed SAMs with different lengths, the work function of silver can be increased from 4.3 eV for the bare silver metal to 5.3 eV for modified silver without compromising the wetting/spreading of emissive conjugated polymer for PLED.

With proper SAM-modified silver as anode, polymeric light-emitting diodes with high efficiency and brightness close to that with ITO/PEDOT:PSS as anode were achieved for both top and bottom emission devices. This offers the opportunity to replace the commonly used but more resistive and expensive indium-tin-oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) anode with the low resistive and low cost silver metal anode for large area PLED and polymer solar cell application.

2. Experimental

Silver substrates were prepared on chromium-primed glass slides by thermal evaporation. The mixed SAM was prepared by submersing Ag substrate into a 1 mM ethanolic solution containing a fluorinated alkanethiol and a carboxyl-terminated alkanethiol in different ratios. The fluorinated alkanethiol used was either 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexanethiol (FHT) or 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanethiol (FOT), and the carboxyl-terminated alkanethiol used was either 8-mercaptooctanoic acid (MOA) or 11-mercaptoundecanoic acid (MUA), all obtained from Aldrich and used without purification. The molecular structures of these SAM-forming components are shown in Fig. 1(c). Reflection–absorption IR spectra were taken with a Biorad FTS-60 Infrared spectrometer equipped with a MCT detector. A custom-designed optics unit with 86° incidence angle and p-polarized light were employed. Plasma-cleaned gold wafer was used as reference for all spectra. Contact angle was taken with a GBX DIGIDROP Goniometer, and Teflon-coated needles were used to dispense water and Toluene as the contacting liquid onto the surface of the monolayers. The data reported are the average of 4–5 drops measured on both sides. The structure of the PLED is Cr/Ag/mixed-SAMs/emission layer/cathode. The Cr is used as the adhesive layer for Ag. The thickness of Cr is 100 Å for top-emitting device and 30 Å for bottom-emitting device. The thickness of Ag is 800 Å for top-emitting device and 150 Å for bottom-emitting device. The substrate was immersed for 1 h before rinsing with absolute ethanol, acetone and blown dry with a pure nitrogen flow. Poly(para-phenylene vinylene, 800 Å) (Super Yellow from Merck) was spin-coated from a toluene solution (0.8 wt.%) as emission layer. The sample was annealed at 80 °C for 20 min in a glove box to remove the residual solvent. The cathode was Ca (100 Å)/Ag (150 Å) for top-emitting devices and Ca (350 Å)/Al (1000 Å) for bottom-emitting devices. ITO/PEDOT:PSS is used as anode for standard device. A 40 nm PEDOT:PSS (CLEVIOS™ P VP AI 4083) layer is spin coated on a cleaned and patterned ITO substrate and annealed at 200 °C in nitrogen for 10 min. The active area of the PLED was 1 mm^2. Electrode deposition was done by thermal evaporation under 10^{-6} torr. The work functions of the SAM-modified Ag surfaces were measured with a photoelectron spectrometer (AC-2, Riken Keiki) in ambient air with a UV source. The work function was calculated by plotting the square root of the total electron counts versus photoelectron energy and extrapolating the linear fit of the counts to zero as described in
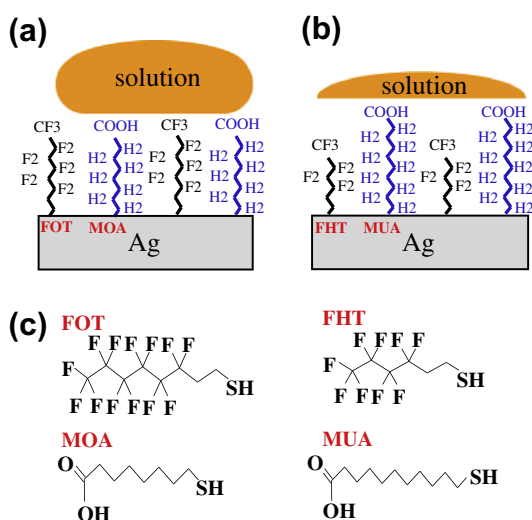

Fig. 1. The schematic plots showing the shapes of the solution drops on the mixed-SAMs with (a) equal molecular lengths and (b) non-equal molecular lengths. (c) Molecular structures of the molecules used for mixed self-assemble monolayer formation.

literature [16]. The current density–voltage (J–V) and luminance–voltage (L–V) characteristics of the devices were measured by Keithly 2400 source meter and spectrophotometer PR650.

3. Results and discussion

Ellipsometry measurement of the mixed monolayer was carried out to confirm the monolayer nature of the co-adsorbed films. For example, in the MUA/FHT system, the measured film thickness varies between 6.5 Å (for single component FHT) and 12.0 Å (for single component MUA), depending on the composition.

Reflection absorption IR spectra were taken for the mixed monolayers as a function of the solution composition. With 8-mercaptooctanoic acid (MOA) mixed with the same chain length fluorinated thiol FOT, the intensity of characteristic absorption for carboxyl group at 1712 cm^{-1} decreases with increasing amount of FOT in the adsorbing solution, whereas that for the characteristic absorptions for C–F stretches between 1350 and 1250 cm^{-1} increase with more FOT in the adsorbing solution (Fig. 2). The surface composition correlates with the solution composition. Similar trends for the IR spectra of mixed monolayers composed of MOA and FHT or MUA and FHT, where the carboxyl-terminated thiol is longer than the fluorinated thiol. Based on the integration of the respective peaks, the surface composition was estimated and plotted versus solution composition, as shown in Fig. 3. The surface composition may deviate from the solution composition. Particularly when the chain lengths are much different. Thus for MUA/FHT system, the longer chain MUA will be more favored on the surface than the shorter chain. For the same chain length mixed system of MOA/FOT, the fluorinated component is more favored, presumably because its lower solubility in the ethanol solvent used [15].

One concern is the possible phase separation of the fluorinated component and the carboxyl-terminated alkyl component. In earlier work for mixed monolayer of fluorinated chain and alkyl chain [13], phase separation is possible but of small scale (tens of nanometers) that it is insignificant in affecting the macroscopic properties such as wetting and work function. In the current case where carboxyl groups are introduced, the potential H-bonding interaction between carboxyl group and fluorinated hydrocarbon [17,18] is expected to alleviate, not aggrevate the problem of phase separation.
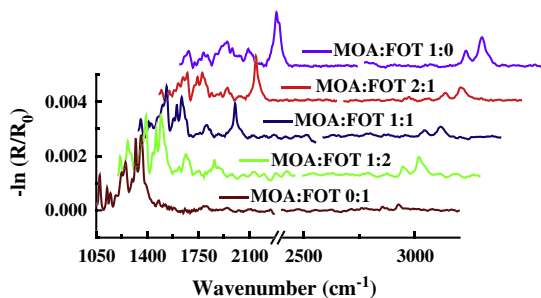
Fig. 2. Reflection–absorption IR spectra of mixed monolayers of MOA (carboxyl-terminated thiol) and FOT (fluorinated thiol) on Ag.
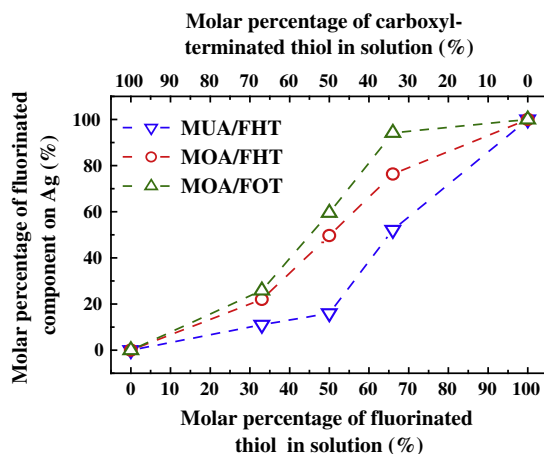
Fig. 3. Plots of surface composition as a function of solution composition, based on the integrated areas under the v_s (CF-) band ($\sim$1350 cm^{-1}) and v_s (C=O in COOH) band ($\sim$1712 cm^{-1}), for the mixed SAMs.

The influences of the molar percentage and chain length of fluorinated and carboxyl-terminated thiols on the wetting property of Ag are shown in Fig. 3(a). On Ag surface covered by a single component MOA or MUA monolayer, the water contact angle is lower than 20°, due to the hydrophilic nature of carboxyl group at the outmost surface. The contact angle increases with increasing amount of fluorinated alkanethiol in the solution. For mixed-SAMs with equal chain length (MOA/FOT), the water contact angle reaches a plateau over 90° as the molar percentage of FOT is higher than 50%.

For Ag surface modified by mixed-SAMs of MOA/FHT, where the carboxyl-terminated thiol is two carbon atoms longer than the fluorinated thiol, the water contact angle increases with increasing ratio of FHT in solution and reaches a plateau as the percentage of FHT is higher than 80%. The wetting property is improved (contact angle decreased) comparing the contact angles at the same mixing ratios. For mixed monolayers prepared from MUA/FHT, where the carboxyl-terminated thiol is six carbon atoms longer than the fluorinated thiol, the contact angle of FHT/MUA-modified Ag surface increases linearly without a plateau and reaches the highest water contact angle around 110° for pure FHT monolayer. This implies the wettability of the MUA/FHT-modified Ag surface is further improved if comparing the contact angles at the same mixing ratios in solution. Longer carboxyl-terminated thiol seems to shield the hydrophobic component down under and rendering the surface relatively more "hydrophilic".

Wettability relates to the sticking property of a polymer by spin-coating. In this work, it was found that formation of polymer film by spin-coating is impossible or very difficult when the substrate surface is highly hydrophobic (for example, the water contact angle is higher than 90°). The polymer solution tends to slip away from the substrate while the substrate spins. It is noted that toluene is used as the solvent for the polymer solution. Similar wetting behavior for toluene on the modified surface was observed (Fig. 4). For the equal length MOA/FOT mixed
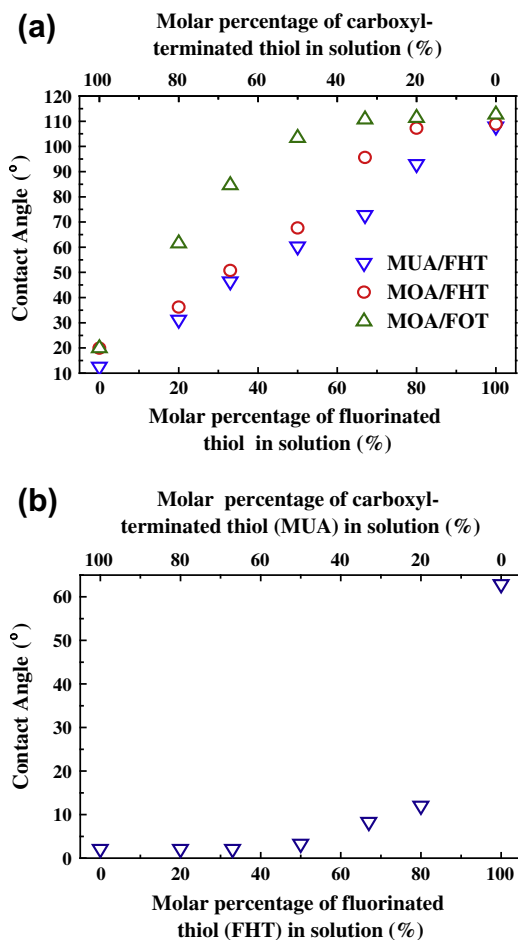
(a)

(b)

Fig. 4. (a) The water contact angle on mixed SAMs-modified Ag. FHT and FOT are fluorinated alkanethiol with six and eight carbon atoms, respectively. MOA and MUA are carboxyl-terminated alkanethiol with eight and eleven carbon atoms, respectively. (b) The toluene contact angle on mixed SAMs containing MUA and FHT on Ag.

Fig. 5. The work function of mixed SAMs-modified Ag. FHT and FOT are fluorinated alkanethiol with six and eight carbon atoms, respectively. MOA and MUA are carboxyl-terminated alkanethiol with eight and eleven carbon atoms, respectively.

monolayer-modified Ag, the polymer cannot be spun on as the amount of FOT is higher than 50%. For the Ag surface modified by MUA/FHT monolayer, the wetting property of the surface is improved as stated above. Higher percentage of FHT is allowed before the surface becomes too hydrophobic to retain the polymer upon spin coating. The higher amount of FHT serves to increase the work function and reduce the hole injection barrier.

SAM-induced work function change was measured by AC2 in ambient, as shown in Fig. 5. The work function of bare Ag is 4.3 eV (compare to a value of 4.4 eV reported in literature [10]). For Ag modified with carboxyl-terminated SAM (MOA or MUA), the work function increases to about 4.9–5.0 eV which is still not sufficient for hole injection into most luminescent polymers. By increasing the amount of fluorinated component in a mixed monolayer, the work function of the modified Ag now can be tuned. It is noted that for MOA/FHT or MUA/FHT systems, where the carboxyl-terminated chain is longer than the fluorinated chain, the work functions initially remained similar or even decreased until the
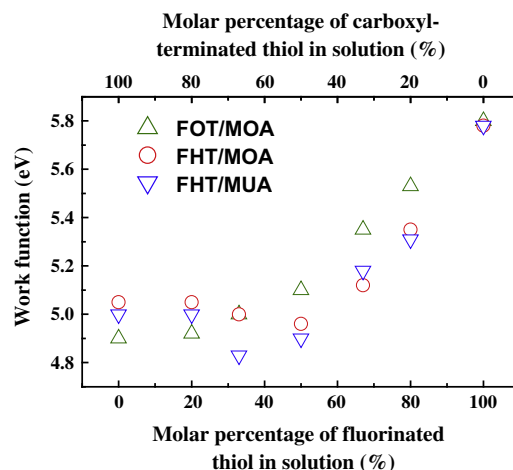
solution percentage for fluorinated component is more than 50%, when the work function increased steadily, up to around 5.8 eV as the amount of fluorinated component is 100%. This value is somewhat higher than the 5.5 eV reported for perfluorinated C10 alkanethiol monolayer on Ag [10]. With equal length MOA/FOT monolayer as modifier, no such dip in work function was observed. The initial decrease of the work function may be due to the re-orientation of the carboxyl groups at the interface. Nevertheless, the amount of FOT is limited to well below 50% to give acceptable wettability for spin-coating to work. This will limit the work function to be below 5.0 eV. With fluorinated component shorter than the carboxyl-terminated component, higher amount of fluorinated component is allowed to give acceptable wettability and the work function can be increased up to 5.3 eV, which is favorable for reducing charge injection barrier.

To further demonstrate the continuous work function change of mixed-SAM-modified Ag surfaces indeed influence the hole injection property of Ag electrode, the current density (J)–voltage (V) relationship of hole-only diodes are compared. J–V curves of the device in the structure Cr/Ag/mixed SAMs (FHT/MUA)/super yellow (SY) or poly(3-hexyl thiophene) (P3HT)/Al are demonstrated in Fig. 6. SY and P3HT layers are fabricated by blade and spin coating technique [19,20]. The blade and spin coating technique can be utilized to deposit a film on all mixed-SAM-modified Ag electrodes no matter the wetting property of the metal. The highest occupied molecular orbital (HOMO) of P3HT and SY are 5.1 and 5.4 eV, respectively. For the P3HT diode, J increases as the FHT ratio increases from 0% to 66%. However, J of devices with 66% and 80% FHT are similar. This is attributed to the work function of FHT modified Ag electrodes with FHT ratio larger than 66% are higher than the HOMO level of P3HT and hence forming an Ohmic contact between electrode and P3HT. As for the diode made by SY with higher HOMO level, J increases as the FHT ratio increases from 0% to 80%. This
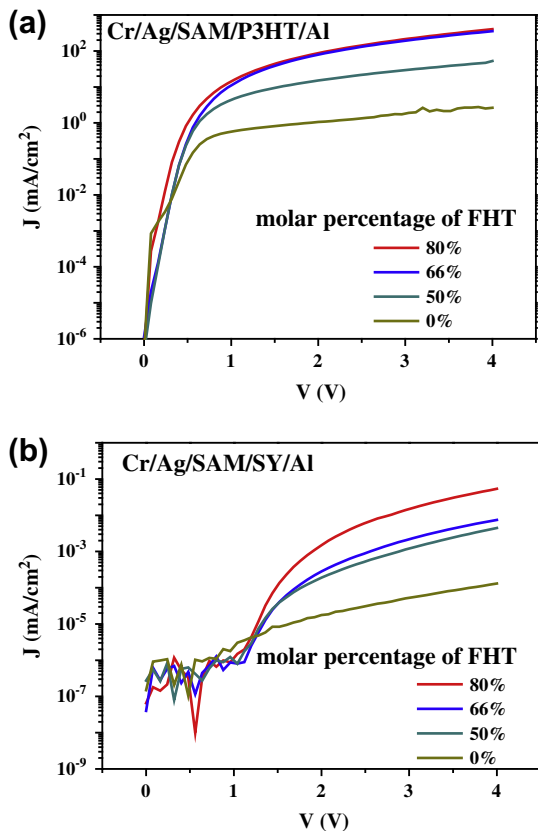
Fig. 6. The current density as a function of voltage of the hole-only devices made by (a) P3HT and (b) super yellow.

demonstrates that the mixed-SAM indeed modifies the work function continuously which is suitable serving as an anode.

The effect of mixed SAM-modification on charge injection is demonstrated by a bottom-emitting PLED, as shown in Fig. 7. The current density at same bias increases with increasing amount of FHT in the monolayer, presumably due to the increase in work function of FHT/MUA-modified Ag. The maximum current efficiency of the devices with 80%, 66%, 50% FHT is 4.5 cd/A (at 5 V), 2.1 cd/A (at 7 V), and 1.2 cd/A (at 9 V), respectively. The maximum luminance of the device with 80% FHT is higher than 40,000 cd/m^2 at 10 V. This demonstrates the mixed SAMs-modified Ag can be used as anode to replace ITO. Standard device with ITO/PEDOT:PSS anode is also fabricated for comparison. The standard device achieves a maximum current efficiency of 7.1 cd/A at 6 V. The lower efficiency in the device with 80% FHT results from the reduced transparency of the anode (30 Å Cr/150 Å Ag) as shown in Fig. 8. The top-emitting PLED with FHT/MUA-modified Ag as anode is also fabricated and its characteristics are shown in Fig. 9 (a) and (b). The current density at same bias also increases with increasing amount of FHT. The maximum current efficiency of the devices with 80%, 66%, 50% FHT is 6.7 cd/A (at 6 V), 3.7 cd/A (at 7 V), and 0.8 cd/A (at 8 V), respectively. The maximum luminance of the device with 80% FHT is also
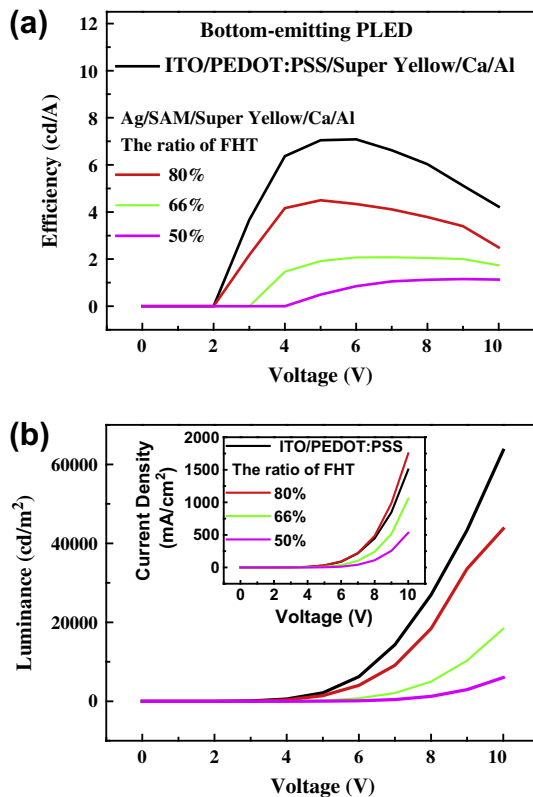

Fig. 7. Characteristics of bottom-emission polymer light-emitting diodes with the structure of anode/super yellow/Ca/Al. FHT/MUA mixed-SAMs-modified Ag and ITO/PEDOT:PSS are utilized as anode. (a) The current efficiency as a function of voltage. (b) The luminance as a function of voltage. The inset shows the current density as a function of voltage.
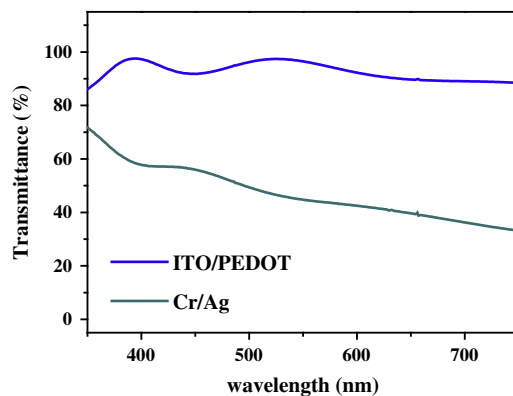

Fig. 8. The optical transmittance of ITO/PEDOT and Cr/Ag electrode.

higher than 40, 000 cd/m^2 at 10 V. Finally, a top-emitting green phosphorescence PLED is also fabricated with FHT/MUA-modified Ag as anode. The emission layer is a blend of tris[2-(p-tolyl)pyridine]iridium(III) (Ir(mppy)$_3$), N,N′-bis(3-methylphenyl)-N,N′-bis(phenyl)-benzidine (TPD), 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) into poly(vinylcarbazole) (PVK, Mw = 1100,000) in the weight ratio of 6:9:24:61. Some spike can be observed in the current density–voltage curve shown in Fig. 9(c)
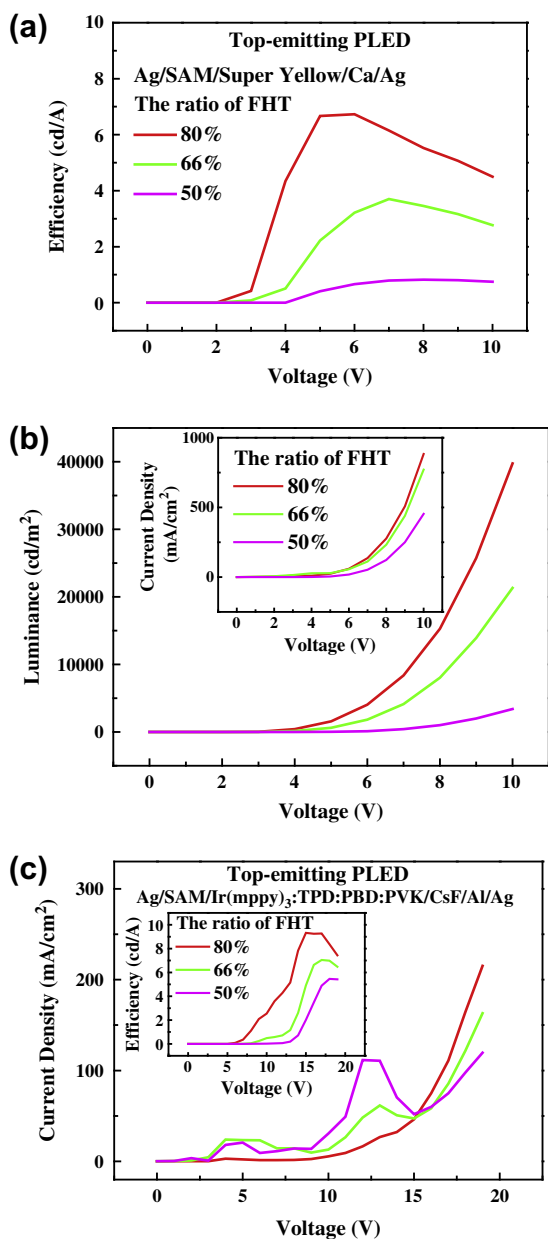
Fig. 9. Characteristics of top-emission polymer light-emitting diode with the structure of Cr/Ag/SAM/super yellow/Ca/Ag. FHT/MUA mixed-SAMs-modified Ag electrodes are utilized as anode. (a) The current efficiency as a function of voltage. (b) The luminance as a function of voltage. The inset shows the current density as a function of voltage. (c) Current density–voltage plot of top-emission polymer light-emitting diode with the structure of Cr/Ag/SAM/Ir(mppy)₃:TPD:PBD:PVK/CsF/Al/Ag. The inset shows the current efficiency as a function of voltage.

which may result from current leakage path. The current efficiency is 9.3 cd/A at 15 V. The leakage path may results from the pinhole or aggregation of the component which formed during spin coating. Interaction between SAM-modified Ag surface and polymer solution plays an important role during spin coating process.

4. Conclusion

In conclusion, mixed monolayers of a fluorinated alkanethiol and a carboxyl-terminated alkanethiol of different chain lengths can be used to decouple the effect on the work function and surface wetting for silver. Using a longer carboxyl-terminated component, which may shield or and bury the shorter fluorinated component in the SAM allows higher amount of fluorinated component to be used for increasing the work function of silver, without compromising the wetting property of the substrate needed for spin-coating of emissive conjugated polymer for PLED. PLED with high efficiency and brightness close to the case of ITO/PEDOT:PSS anode are achieved for both top and bottom emission PLED. The tunability in both work function and wettability of silver electrode offers more flexibility in device design.

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