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Molecular monolayer modification of the cathode in organic light-emitting diodes

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The effects of alkanethiol self-assembled monolayers (SAMs) attached to the gold cathode of organic light-emitting diodes made by soft contact lamination are investigated. In spite of reported work function lowering by alkanethiol SAMs, the results from this work showed that their primary effect in carrier transport is to act as a thin insulating layer, causing current reduction. At the same time, the luminescence efficiency was enhanced because the SAMs reduce exciton quenching by the metal cathode. A two-order-of-magnitude enhancement at light emission onset was observed for a hexadecanethiol modified device. © 2006 American Institute of Physics. [DOI: 10.1063/1.2397033]

Understanding interfaces between inorganic electrodes and active organic materials is critical to the improvement of the performance of organic electronic and optoelectronic devices.¹ Recently, interface modification of the electrodes in organic light-emitting diodes^{2–5} (OLEDs) and organic thin-film transistors^{6,7} (OTFTs) has been shown to enhance electroluminescence efficiency in OLEDs by reducing the hole injection barrier and to improve carrier mobility in OTFTs by reducing contact resistance. One of the most attractive approaches to modifying electrodes employs self-assembled monolayers (SAMs) because their electronic and chemical properties can be tuned through synthesis and there exist many well-characterized systems. It is well known that SAMs can increase or decrease electrode work function depending on the sign of the dipole layer.^{2,5,8,9} Such a work function change on the anodes has been shown to alter hole injection efficiency.^{2,4,9} While work function changes have been widely investigated, other factors associated with SAM modification have not been thoroughly studied. These include reduction in carrier transmission arising from inserting an insulating layer, voltage drop across the insulating molecular layer resulting in the lowering of the effective energy barrier height between the injection electrode and the organic semiconductor, and reduction or removal of exciton quenching pathways. Moreover, due to the conventional layer-by-layer fabrication methods, most existing studies have been done by modifying bottom anodes.^{2,4,9} Here, we examine the effect of alkanethiol SAM modification of the top cathode. The experiment was made possible because we employ an unconventional approach, soft contact lamination (ScL), to construct OLEDs.¹⁰

Conventionally, the top electrodes (cathodes) of OLEDs are deposited by vacuum deposition of appropriate metal(s) onto the active organics. Most work to date for cathode modification was done using inorganics such as metal fluorides and Al₂O₃,^{11–13} which are also vacuum deposited on top of the active organic layer. While this approach was shown to improve OLED efficiency, the vacuum deposition

creates a poorly controlled interface. Furthermore, the layer-by-layer vacuum deposition does not permit using molecules to modify the top electrode. In contrast to conventional fabrication methods, the OLEDs are constructed in two steps in ScL: the electroluminescent (EL) polymer is spin cast on the bottom anode, indium tin oxide (ITO) covered glass slides,¹⁴ while the top Au cathode is deposited on an elastomeric substrate, poly(dimethylsiloxane) (PDMS) (Sylgard 184, Dow Corning Inc.). The OLEDs are completed by conformally laminating the two parts together. Figure 1(a) illustrates the ScL process schematically. In this experiment, we use a green-emitting polyfluorene derivative (Dow LUMATION Green B, Dow Chemical Co.)¹⁵ as the EL polymer (100 nm thick). The PDMS coated with gold electrodes was prepared according to previously reported procedures.¹⁰ As evident from Fig. 1(a), the Au electrode surface is readily accessible and can be chemically modified. In this study, we used three different alkanethiol lengths [CH₃(CH₂)_nSH: *n*=7, 11, and 15, hereafter C8, C12, and C16], which readily self-assemble on Au. We exposed the Au electrode to 2 mM alkanethiol ethanolic solution for 15 min, after which the electrode was rinsed with ethanol and dried with N₂. The lamination is facilitated by van der Waals forces only and is reversible. Hence, these SAM modified ScL OLEDs have an abrupt interface between the EL polymer layer and the cathode.

Figure 2(a) shows the current density versus voltage characteristics of a reference OLED made by ScL with a bare Au electrode and of the ScL OLEDs with alkanethiol SAM modified Au cathodes. For SAM modified devices, the current at a given voltage was reduced for voltages below 12 V. The longer the molecules,¹⁶ the more the current reduction was observed. Figure 2(b) shows that the output luminescence of OLEDs with SAM modified Au cathodes is enhanced over the reference device with a bare Au cathode. However, the enhancement is reduced as the chain length of the molecules increases. The turn-on voltage of the C8 modified device was reduced to ~8.0 V from that of the bare Au device (~9.3 V). The turn-on voltages increase as the chain length increase (~9.0 eV for C12 modified device and ~10.0 V for C16 modified device). Figure 2(c) displays the current density dependence of the external quantum effi-

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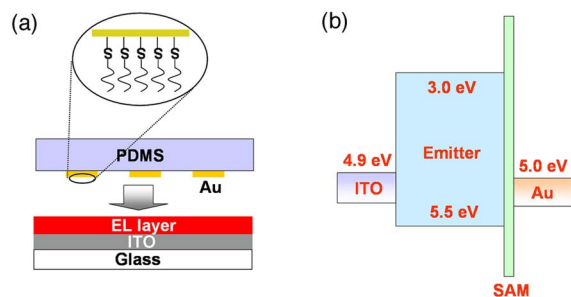


FIG. 1. (Color online) Schematic illustration of (a) an organic light-emitting device made by soft contact lamination (ScL) with molecularly modified Au electrode supported on the poly(dimethylsiloxane) (PDMS) and (b) the energy band diagram without bias. The emitting layer is a green-emitting polyfluorence derivative that was deposited on ITO/glass substrates.

ciency (EQE). The EQEs of SAM modified OLEDs show a weaker current density (or electric field) dependence than that of the bare Au-cathode device. Moreover, the EQEs of SAM modified devices were all higher for current densities below 4 mA/mm^2 (for example, 30–120 times at 0.001 mA/mm^2 and 21–32 times at 0.01 mA/mm^2), but were the same at 4 mA/mm^2 and above. Also, all SAM modified devices have approximately the same EQE above 0.01 mA/mm^2 .

A common interpretation of the results presented in Fig. 2 is that the current reduction is a consequence of hole blocking and that the luminescence enhancement arises from enhanced electron injection, e.g., work function lowering due to SAM modification.^{2,8} We will show that this is not the correct interpretation. Instead, reduction of exciton quenching by blocking exciton diffusion and decreasing nonradiative energy transfer to the Au is the primary mechanism behind improved EQEs in SAM modified devices. It was reported previously that the work function of Au surfaces modified with alkanethiols was independent of chain length for molecules longer than octanethiol.⁸ Hence, the effect of alkanethiol chain length on the work function is not likely to be the dominant factor and will not be considered in the discussions below. A thin hole-blocking and electron-injecting layer would result in increased current and luminescence, as was observed using ionic insulating polymers¹⁷ or insulating Al_2O_3 .¹¹ In these cases, the EQE at all biases (or current densities) would be higher than devices without the hole-blocking and electron-injecting layers due to better charge balance in the active region. In our devices, we observed that EQEs of SAM modified devices are not higher than, but about the same as, that of the bare Au device at high bias. Thus, the primary effects of SAMs in our OLEDs is not hole blocking and enhanced electron injection. Since alkanethiol molecules have large band gaps ($\sim 8 \text{ eV}$), tunneling through this insulating layer is necessary for electrons and holes to transport through the devices and results in current reduction. This effect has been reported previously in other OLED systems.^{18,19} Figure 2(a) inset shows current density versus methylene unit at 6, 9, and 12 V for the three alkanethiol molecules. The decay constant is approximately $\sim 0.37/\text{CH}_2$, which is consistent with reported values for tunneling through alkanethiol molecules at high biases.²⁰

We now consider reduced exciton quenching pathways as the primary effect of the SAMs in these Au-cathode devices. Because of the poor electron injection arising from the use of a high work function cathode, electron-hole recombi-

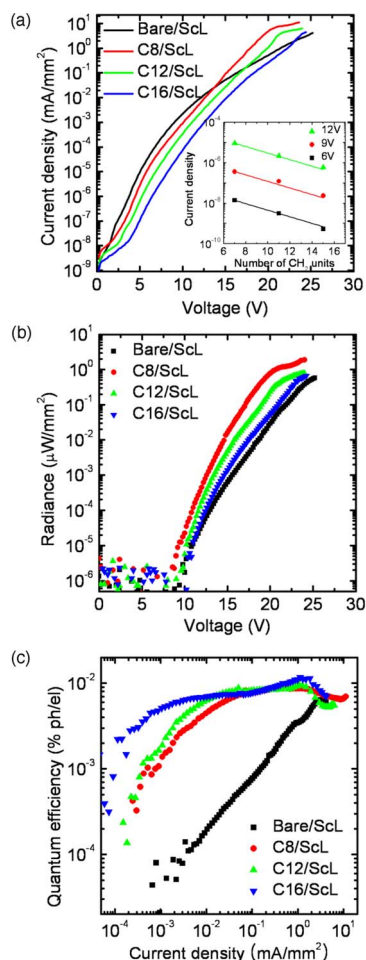


FIG. 2. (Color online) (a) Current density vs voltage, (b) luminance vs voltage, and (c) external quantum efficiency vs current density of soft contact laminated (ScL) OLEDs with bare Au electrode and Au electrodes (20 nm) treated with thiol $[\text{CH}_3(\text{CH}_2)_n\text{SH}]$ molecules (C8, C12, and C16). Inset of (a): Current density vs the number of CH_2 units at 6, 9, and 12 V.

nation in the device at low bias voltages takes places as soon as electrons are injected from the cathode so that most of the excitons are formed near the cathode. Luminescence quenching can occur because of nonradiative energy transfer to the Au cathode via dipole coupling (Förster transfer).²¹ This energy transfer leads to a gradient in the exciton density, which induces excitons to diffuse into the depleted region at the emitting polymer/Au interface.²² Hence, strong quenching occurs within a few nanometers of the Au cathode, especially at low biases near the light-onset voltage. As the field increases, the recombination zone moves away from the cathode interface,²³ which leads to the reduction of nonradiative energy transfer and exciton diffusion to the cathode and hence reduction of exciton quenching.

The nonradiative Förster energy transfer rate (b_{ET}) depends strongly on the distance from the metal,²¹

$$b_{\text{ET}} = \beta d^{-3}, \quad (1)$$

$$\beta = \frac{3q\lambda^3\Theta}{32\pi^3n_1} \left[\frac{n_2K_2}{(n_1^2 + n_2^2 - K_2^2)^2 + 4n_2^2K_2^2} \right], \quad (2)$$

where q is the fluorescence quantum yield of the emitter, λ is the resonant wavelength, Θ is a geometric factor for the different orientations of molecule with respect to the metal ($\Theta = 1$ for a horizontal dipole, 2 for a vertical dipole, and $4/3$ for

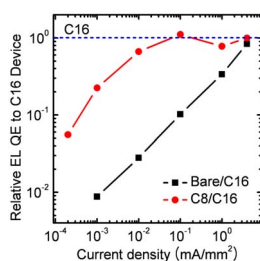


FIG. 3. (Color online) Current density dependence of the relative luminescence yield of the ScL device with the bare Au cathode and with the C8 modified Au cathode with respect to the device with the C16 modified Au cathode.

randomly oriented dipoles), n_1 is the refractive index of the media, and $n_2 + iK_2$ represents the complex index of the metal with the imaginary part K_2 responsible for energy absorption. The first effect of the SAMs is to keep the excitons at a distance at least the thicknesses of the SAM layers away from the cathode, hence reducing exciton quenching. For a β value of $\sim 1.74 \times 10^{-17} \text{ cm}^3$,²⁴ excitons generated at 2.2 nm (C16 chain length) from the Au contact have an approximately ten times lower nonradiative transfer rate than those generated at 1 nm (C8 length) from the Au. Consequently, the exciton density gradient will be lessened and the exciton diffusion rate to the depleted zone will be reduced. If reduced exciton quenching is the primary effect of the SAMs, we expect that a large difference in EQE would exist between devices with SAM modified gold and with bare gold at low electric fields and that this difference would disappear as the field increases. This is precisely what our experimental results show, as seen in Figs. 2(c) and 3. The luminescence yield of the bare Au device was 0.009 of the C16 modified device at $1 \times 10^{-3} \text{ mA/mm}^2$, the current density at the light onset for the bare Au devices. The C8 SAM improved the efficiency at low biases, but the improvement is smaller than C16. This dramatic difference disappears at high biases, under which the recombination zone shifts towards the anode²³ and the maximum EQEs become less sensitive to the presence of SAMs. van Woudenberg *et al.* also reported that OLED efficiency becomes less voltage dependent with reduced exciton quenching.²⁵ These results are consistent with the picture that most of the excitons generated at low bias are located very near to the high work function cathode and are readily quenched by the bare Au. The presence of SAMs reduces this quenching pathway and increases luminescence yield at low voltages.

In summary, we found that the primary effect of alkanethiol SAM modification of the Au cathode in ScL OLEDs is to act as an insulating spacer that reduces exciton quenching by the metal cathode. This conclusion is supported by the enhancement in luminescence at low voltages and the decrease in the voltage dependence of the EQE for SAM modified devices. Near the onset of light emission, the C16 modified device show a two-order-of-magnitude reduction in exciton quenching compared to the bare Au device. This work shows that the effects of electrode modification on device performance are complex. Full understanding can only be achieved from studying the behavior of finished devices, not from changes in electrode characteristics such as the work function.

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