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Electrochemical properties of self-assembled monolayers of tripod-shaped molecules and their applications to organic light-emitting diodes

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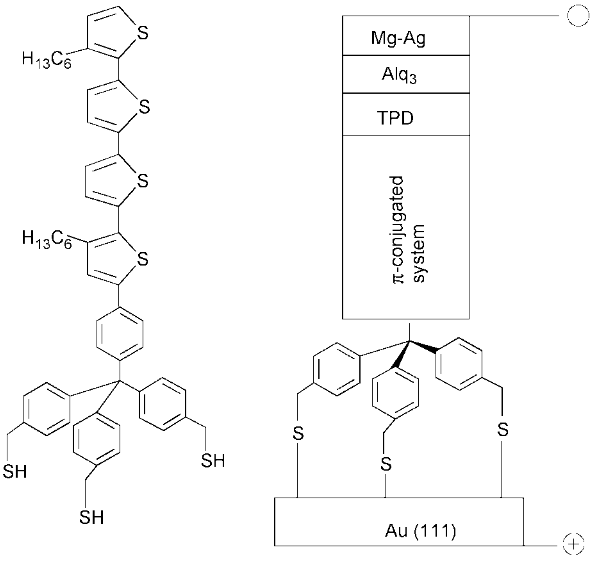
Self-assembled monolayers of a tripod-shaped conjugated-thiol grafted onto Au(111) substrates are found to show electrochemically reversible oxidation and reduction and to improve electroluminescence performances of organic light-emitting diodes.

Self-assembled monolayers (SAMs) are ordered molecular assemblies that are formed spontaneously by the adsorption of organic molecules with a specific affinity of their head-groups on substrates. Unique characteristics of the SAMs lead to their potential applications in many fields such as chemical sensors and OLEDs.[1] From both the fundamental and technological points of view, the SAMs are required to be chemically stable and to show good charge transfer ability in many cases. Compared to conventional molecules with only a single head-group, the molecules with multiple head-groups are expected to produce more structurally stable SAMs. A long π-conjugated segment born in the molecules will facilitate the charge transfer through the whole SAM. Therefore, the SAMs of molecules with a multiple-point anchor and a π-conjugated segment are very promising in charge and energy transfer processes.

In this work, we report electrochemical behavior of SAMs of a tripod-shaped conjugated-thiol, 4T-3SH (Fig. 1a), and investigate for the first time the influences of the SAM of the multiple-point anchoring π-conjugated thiol on the electroluminescence (EL) performances of the Au/TPD/Alq$_3$/Mg-Ag device consisting of the SAM-coated Au electrode as anode (Fig. 1b), where TPD and Alq$_3$ represent *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (a hole transporting material) and tris(8-quinolinolato)aluminium(III) (an emitter), respectively. Before use, the thiol groups in 4T-3SH were protected in the form of acetylthio groups. The protected 4T-3SH was synthesized by a coupling reaction between 5-tributylstannyl-3,3‴-dihexyl-2,2′:5′,2″:5″,2‴-quaterthiophene (for the tail unit) and 4-bromophenyltris(4-*S*-acetylthiomethylphenyl)methane (for the anchor unit) in the presence of Pd(PPh$_3$)$_4$. After being purified with column chromatography on silical gel (eluent: DCM), the resulting yellow semisolid was identified by elemental analysis and ^{1}H NMR and IR spectroscopic analyses. The details of synthesis and the analysis results will be described elsewhere.[2] The as-synthesized protected 4T-3SH was de-protected to obtain solutions of 4T-3SH just prior to preparing the SAMs.



(a) (b)

Fig. 1 (a) Chemical structure of the conjugated-thiol, 4T-3SH, and (b) schematic representation of the Au-SAM/TPD/Alq$_3$/Mg-Ag device.

Au films with thickness of 35 nm were electron beam deposited onto freshly cleaved mica sheets and then annealed at 300 °C for 3 h. X-ray diffraction analysis confirmed that the predominant atomic surface structure for the annealed Au/mica films was that of the (111) indexed plane. SAMs of 4T-3SH were grafted onto the Au(111)/mica substrates by immersing in its deaerated DCM solution (1×10^{-4} mol dm^{-3}) for several hours, followed by thoroughly rinsing with DCM and then ethanol and finally by vacuum drying. The transparency of the Au/mica substrate was about 30% in the visible range. The SAM-coated Au electrode was used to fabricate EL devices with a configuration of Au-SAM/TPD(60 nm)/Alq$_3$(60 nm)/Mg-Ag(200 nm) with a light-emitting area of 10×1 mm^2. The EL characteristics were measured as described previously.[3] Electrochemical measurements were carried out using a three-electrode system. A Pt wire and an Ag/AgClO$_4$ (0.1 mol dm^{-3}) electrode were used as the counter and reference electrodes, respectively.

Cyclic voltammograms of the SAM-coated Au(111) electrode were measured at a scan rate of 100 mV s^{-1} in deaerated dry acetonitrile solutions containing 0.1 mol dm^{-3} LiClO$_4$. As shown in Fig. 2, a pair of oxidation/reduction peaks appeared at 0.55/0.45 V in a potential range from 0 V to 0.65 V. In the voltammogram obtained with an increased positive potential limit, another less reversible oxidation peak occurs at 0.87 V. These anodic and cathodic peaks are ascribable to the oxidation and reduction of the π-conjugated quaterthiophene part in the molecule. Integration of the anodic current over the potential window of the first oxidation peak in the first potential scan gave the coverage of the adsorbed thiol molecules as 2.9×10^{-10} mol cm^{-2}. In consideration of the three-point anchor of 4T-3SH, this coverage is comparable with the value of $9.3(\pm 0.6) \times 10^{-10}$ mol cm^{-2} for compactly-packed SAMs of conventional alkylthiols on Au(111)/mica substrates.[4] This indicates compact packing of the molecules in the SAM of 4T-3SH on the Au substrate. The electrochemical stability of the SAM was

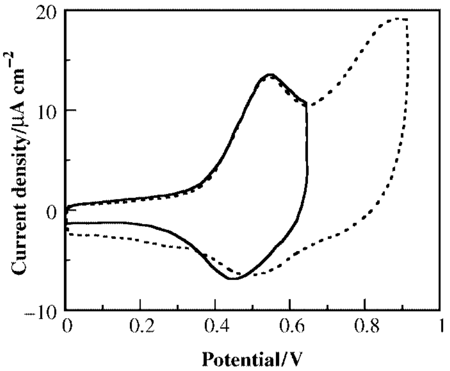


Fig. 2 Cyclic voltammograms of a 4T-3SH SAM grafted on Au(111)/mica substrate with upper potential limits of (solid line) 0.65 and (dotted line) 0.90 V in an acetonitrile solution of 0.1 mol dm^{-3} $LiClO_4$. The potential sweep rate was 100 mV s^{-1}.

evaluated by cyclic voltammetric measurements conducted by potential sweeping from 0 and 0.65 V at 200 mV s^{-1}. The oxidation and reduction peaks were clearly seen after a potential sweeping of 200 cycles, indicative of good stability.

Because of the good stability of the SAM and the existence of the π-conjugated quaterthiophene tail in 4T-3SH, the SAM is expected to facilitate the charge transfer when it is installed in EL devices. Fig. 3 illustrates current–voltage (*I*–*V*) and luminance–voltage (*L*–*V*) characteristics of the Au/TPD/Alq_3/Mg-Ag devices with and without SAM. Compared to the devices without the SAM, both the *I*–*V* and *L*–*V* curves of the device with the SAM shift considerably to the low voltage direction. For example, the operating voltage at a luminance of 100 cd m^{-2} decreases from 9.5 V for the Au/TPD/Alq_3/Mg-Ag device to 6.3 V for the Au-SAM/TPD/Alq_3/Mg-Ag device. This large reduction in the operating voltage is possibly related to the combination of a tripod-shaped head-group and a large π-conjugated system in 4T-3SH in the following aspects. (1) The tripod-shaped three-point anchor increases the structural stability of the SAM on the Au substrate. (2) The adhesion between the SAM and the TPD layer is increased. (3) The π-conjugated quaterthiophene tail promotes charge transfer from the Au anode to the TPD layer. (4) The symmetry of tripod-shaped molecules with rigid π-conjugated backbone suggests that the molecule stands normal to the Au/mica surface. This increases the effective dipole moment across the SAMs along the surface normal on mica/Au. The dipole moment across SAMs has been reported to influence the work function of the metal substrate,[5] the charge injection at the electrodes,[6] and EL performances of OLEDs.[7] We measured the work function of the Au(111) surface before and after the SAM-coating using a home-made Kelvin probe apparatus.[8] It was found that the work function of the SAM-coated Au increased by about 0.4 eV compared to the Au electrode without SAM. The increased apparent work function of the SAM-coated Au will bring about a reduction of the hole injection barrier height. Our result is different from the report of Campbell and coworkers,[6] who found that a conjugated-thiol ($HS\text{-}(C_6H_4C_2)_2C_6H_4\text{-}H$) led to decreased work function of the metal substrate and depressed hole injection, although its derivative $HS\text{-}(C_6H_4C_2)_2C_6H_4\text{-}F$ increased the work function of the metal anode and the hole injection from the anode.[6] Further investigation is in progress for better understanding of the role of the SAMs in the OLEDs.

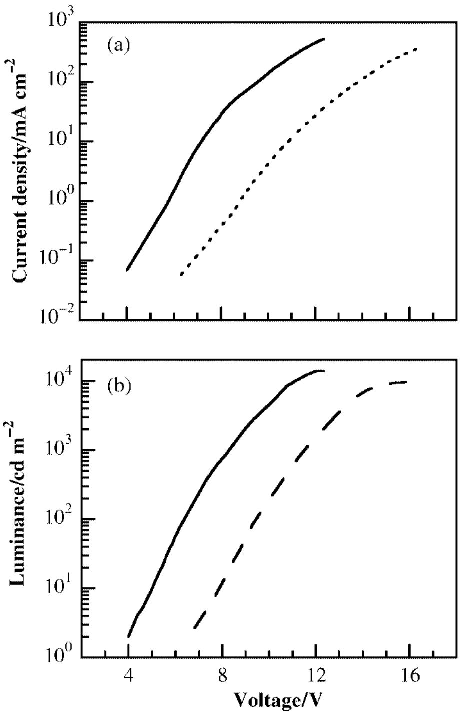


Fig. 3 (a) Current–voltage and (b) luminance–voltage characteristics of Au–SAM/TPD/Alq_3/Mg-Ag (solid line) and Au/TPD/Alq_3/Mg-Ag (dotted line) devices.

In conclusion, molecules of 4T-3SH have been grafted onto a Au(111) surface to produce compact packing SAMs. Its three-point anchor increases the stability of the SAM, and the quaterthiophene tail leads to reversible oxidation and reduction. The SAM has been found to enhance the charge injection at the Au anode of the EL devices. Consequently, the Au-SAM/TPD/Alq_3/Mg-Ag device has a much lower operating voltage than the Au/TPD/Alq_3/Mg-Ag device.

Notes and references

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