

Polymer–perovskite blend light-emitting diodes using a self-compensated heavily doped polymeric anode ^{EP}

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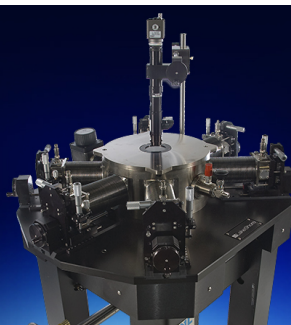
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ABSTRACT

Perovskite-based light-emitting diodes (PeLEDs) are drawing great attention due to their remarkable performance and ease of processing. Nevertheless, a critical aspect is the perovskite film formation on top of solution-processed anodes such as poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). Use of conventional PEDOT:PSS anodes gives rise to high leakage currents that mask the hole transport properties of the perovskite semiconductor. Here, we show a feasible approach to overcome this constraint by implementing a solution-processed, self-compensated, hole-doped triarylamine-fluorene copolymer (*p*-pTFF-C₂F₅SIS) with a work function of 5.85 eV as the anode for polymer-perovskite blend LED devices. Highly efficient hole injection was obtained, near that of evaporated MoO_x. Hole-only devices reveal that the hole transport in the polymer-perovskite blend is trap-limited. PeLEDs with the ultrahigh-workfunction *p*-pTFF-C₂F₅SIS anode show much lower leakage and much better stability in current-voltage and light output characteristics than those with the PEDOT:PSS anode.

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Metal halide perovskites have recently emerged as promising candidates for solution-processed optoelectronics, including solar cells, photodetectors, and light-emitting diodes (LEDs).^{1–3} Perovskites have recently attracted much attention for their use in LEDs due to their high photoluminescence quantum efficiency, high color purity, thermal stability, and tunable bandgap.^{4–6} In the past five years, perovskite-based light-emitting diodes (PeLEDs) have witnessed unprecedented progress in terms of external quantum efficiency (EQE), which exceeded the milestone of 20%.^{7–9} One of the most efficient approaches to simultaneously suppress non-radiative recombination and enhance radiative emission processes in PeLEDs, relies on the employment of low-dimensional structures to confine charge carriers.^{9–11} Many low-dimensional perovskite structures employed for high-performance

devices have deep valence bands (VB).^{10,12–14} Therefore, high work function (WF) hole injection layers (HILs) are needed to ensure ohmic contacts. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) is the conventional HIL used in solution-processed optoelectronic devices because of its ease of processability and versatility. However, PEDOT:PSS has a WF close to 5.0 eV,¹⁵ which creates large hole injection barriers in LEDs based on perovskites that have considerably deeper valence band energies. Hence, the potential of PeLEDs cannot be fully exploited since the magnitude of the injected current exponentially decreases with the injection barrier.¹⁶ Alternatively, self-organized conducting polymers or metal oxides with larger WFs can be employed to obtain a hole contact with lower barriers.^{17–19} However, aggregate formation and wettability mismatches with the subsequently coated

perovskite active layer easily results in uneven coatings, which are detrimental to device performance. Recently, strong dopants have been used to yield self-compensated, hole-doped conjugated polyelectrolytes with ultrahigh WFs.²⁰ Films of these ultrahigh-WF conjugated polymers have been used to achieve ohmic contacts with organic semiconductors with large ionization energies. However, their use in perovskite optoelectronic devices has yet to be explored. In this work, we demonstrate the successful integration of a solution-processed polymeric HIL with a WF of 5.85 eV in quasi-two-dimensional/three-dimensional (2D/3D) perovskite-polymer bulk heterostructure LEDs (PePoLEDs). The polymeric HIL is based on a triarylamine-fluorene copolymer with a larger ionization energy that produces a large WF in the hole-doped state. Its implementation in PePoLEDs results in strong suppression of the leakage current that impairs devices using PEDOT:PSS as HIL. Moreover, its implementation also greatly improved the operational stability of PePoLEDs to over three weeks.

The triarylamine-fluorene copolymer is poly(9,9-bis(3-(pentafluoroethanesulfonyl-imidosulfonyl)propyl)fluorene-2,7-diyl-alt-1,4-phenylene-(*p*-trifluoromethylphenylimino)-1,4-phenylene) sodium salt (pTFF-C₂F₅SIS), which was synthesized according to Suzuki coupling procedures, as described in the [supplementary material](#). The chemical structure is given in [Fig. 1\(a\)](#). Substitution of the pendant ring of the triarylamine unit provides a chemically tunable ionization energy over a 1-eV wide range.²¹ Here, the *p*-trifluoromethyl substitution produces a large ionization energy of 5.85 eV, which results in a WF also of ~5.85 eV for the self-compensated, heavily hole-doped state. It is worth noting that

this state is produced by deliberate hole doping with a strong acceptor, nitrosonium hexafluoroantimonate (NOSbF₆), and internal ion exchange to remove free mobile ions as salt. The holes are counter-balanced by the tethered pentafluoroethylsulfonylimidosulfonyl anions, completely suppressing “doping migration.” To evaluate the suitability of this HIL in LEDs based on a perovskite, we implemented a spin-coated *p*-doped pTFF-C₂F₅SIS film on top of glass/indium tin oxide (ITO) substrates and compared these to devices using PEDOT:PSS as HIL [[Fig. 1\(b\)](#)].

The emissive heterostructure was composed of a 4:1 blend of quasi-2D/3D perovskites and a wide bandgap polymer ($E_g = 4.96$ eV), poly(2-hydroxyethyl methacrylate) (poly-HEMA). The low-dimensional perovskite consisted of 1-naphthylmethylammonium-formamidinium lead iodide [(NMA)₂(FA)_{*m*-1}PbI_{3*m*+1}] with $m > 1$, which exhibits a VB as deep as 5.9 eV.¹⁰ Perovskite-polymer bulk heterostructures have been used to effectively eliminate non-radiative recombination pathways in PeLEDs, giving near 100% internal quantum efficiencies.⁹ In our simple device structure, consisting of ITO/HIL/PePo/LiF/Al, electrons are transferred from the cathode to the conduction band (CB) of (NMA)₂(FA)_{*m*-1}PbI_{3*m*+1}, while holes are injected from PEDOT:PSS or *p*-pTFF-C₂F₅SIS into the VB of (NMA)₂(FA)_{*m*-1}PbI_{3*m*+1}. The radiative recombination between holes and electrons inside the perovskite layer leads to the emission of red light ([Fig. S1, supplementary material](#)).

As a first step, we have investigated the hole injection and transport characteristics by building hole-only devices. In such devices, the current is carried exclusively by holes, preventing electron injection by embedding the emissive layer between two HILs. Hence,

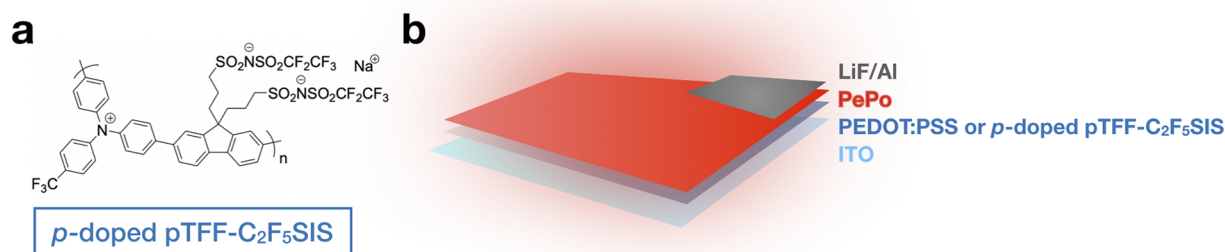


FIG. 1. (a) Chemical structure of pristine pTFF-C₂F₅SIS copolymer. (b) Schematic illustration of PePoLEDs with PEDOT:PSS or *p*-pTFF-C₂F₅SIS as HIL.

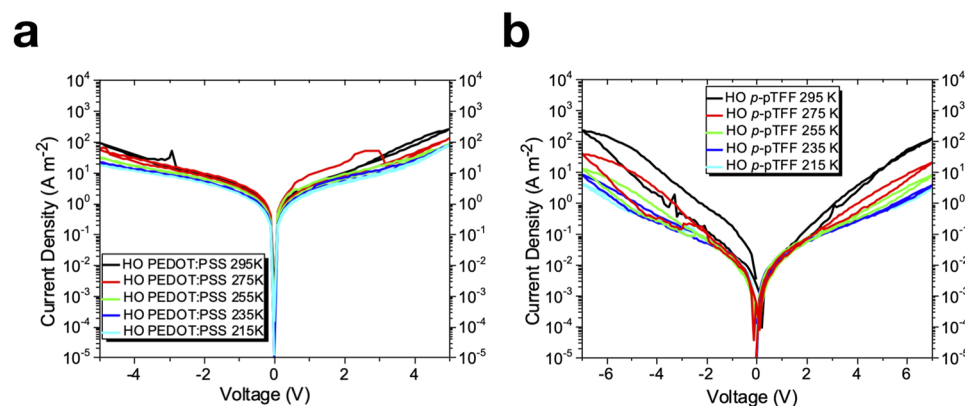


FIG. 2. (a) Current density–voltage characteristics of hole-only devices with PEDOT:PSS and (b) *p*-pTFF-C₂F₅SIS at different temperatures. Negative bias corresponds to hole injection from MoO₃, and positive bias to hole injection from PEDOT:PSS and *p*-pTFF-C₂F₅SIS, respectively.

in our study, the perovskite-polymer bulk layer with a thickness of 180 nm was sandwiched between a PEDOT:PSS or *p*-pTFF-C₂F₅SIS bottom HIL and a thermally evaporated molybdenum oxide (MoO₃) capped with Al as top HIL, as illustrated in Fig. S2. In Fig. 2, the current-density voltage (*J*-*V*) characteristics are shown for the hole-only devices with PEDOT:PSS (a) and *p*-pTFF-C₂F₅SIS (b) as anode.

At first sight, the room temperature characteristics seem relatively similar, with both the PEDOT:PSS and *p*-pTFF-C₂F₅SIS devices reaching current densities of ~ 100 A/m² at 5 V, which contradicts with the lower work function of PEDOT:PSS as compared to *p*-pTFF-C₂F₅SIS. However, care should be taken to assure that the measured current is intrinsic and not dominated by parasitic leakage currents. Such leakage currents typically arise from discontinuities in the active layer (atomic force microscopy images in Fig. S3), which enables locally direct contact between the anode and cathode. The way to discriminate between parasitic leakage current and intrinsic device current is by investigating their temperature dependence.²² As shown in Fig. 2(a), the device with the PEDOT:PSS anode shows a nearly temperature independent current, which is characteristic of a leakage current. In contrast, the devices with the *p*-pTFF-C₂F₅SIS anode are only dominated by leakage currents below 2 V. The leakage current density at 2 V is *ca.* 10 μ A cm⁻², a hundredth of that for the PEDOT:PSS anode. At voltages above 2 V, the device current exceeds the leakage current for the *p*-pTFF-C₂F₅SIS anode, exhibiting a temperature-dependent hole current in the range between 295 K and 215 K [Fig. 2(b)]. The hole current injected from *p*-pTFF-C₂F₅SIS also nearly matches that from MoO_x, but with smaller hysteresis. This allows us to further investigate the hole transport properties of the (NMA)₂(FA)_{*m*-1}Pb_{*m*}I_{3*m*+1}: poly-HEMA blend. At higher voltages, the current density shows a power law dependence on the voltage, $J \sim V^5$ (Fig. 3), which is characteristic of a trap-limited current.²³ Using a drift-diffusion solver,²⁴ the hole current could be modeled using hole traps that are exponentially distributed in energy,²³ with the amount of hole traps given by $P_t = 1.6 \times 10^{24}$ m⁻³ and a trap temperature of 1800 K, which is a measure of the width of the exponential distribution of trap states. Furthermore, for the hole mobility, a value of 4×10^{-8} m² V⁻¹ s⁻¹ was found.

As a next step, we investigate the electrical characteristics of PePoLEDs with PEDOT:PSS and *p*-pTFF-C₂F₅SIS anodes (the device performance parameters are summarized in Table S1). As

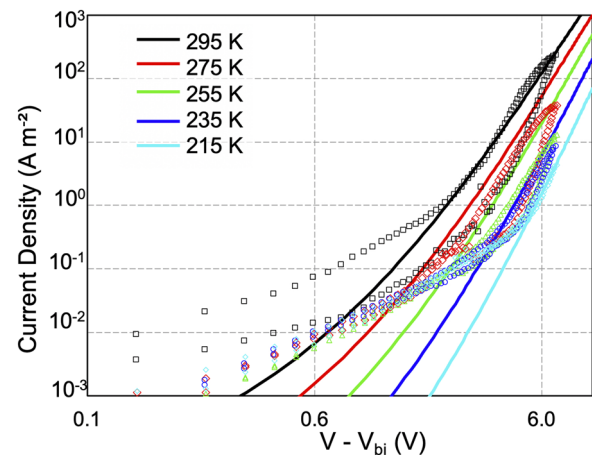


FIG. 3. Current density-voltage characteristics of hole-only devices (symbols) with the *p*-pTFF-C₂F₅SIS anode at different temperatures. The solid lines represent the fit with the numerical drift-diffusion model, including hole traps that are exponentially distributed in energy.

shown in Fig. 4(a), the current density-luminance-voltage characteristics of the PePoLED with PEDOT:PSS as HIL are affected by a high leakage current, similar to the observations made for the hole-only devices in Fig. 2. The high leakage current can be directly observed from the fact that the *J*-*V* characteristics are symmetric, with the expected diode rectification of the current being completely absent. In contrast, PePoLEDs with the *p*-pTFF-C₂F₅SIS anode show working devices with proper diode behavior [Fig. 4(b)]. This demonstrates that *p*-pTFF-C₂F₅SIS is a superior HIL compared to PEDOT:PSS. In addition, the current density profiles of the devices exhibit apparent counterclockwise hysteresis, which typically originate from slow-moving ions.²⁵ Under the application of an electric field, ions drift and pile up at the injecting contact creating a large electric field, which enhances the injection. Therefore, higher currents at the back scan arise. In contrast, clockwise hysteresis originates from trapped charges, which reduce the injection of charges due to electrostatic restrictions.²⁶

In addition, we have evaluated the short-term shelf-life stability of PePoLEDs with the two HILs. The *J*-*V* characteristics of

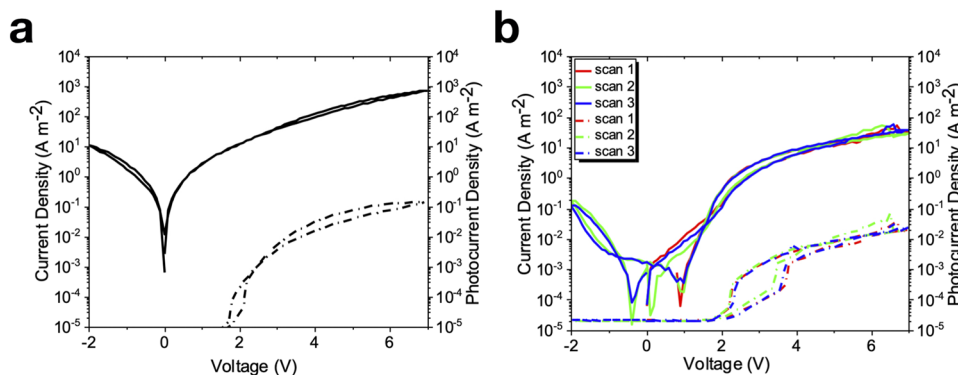


FIG. 4. Current density-voltage-photocurrent density characteristics of PePoLEDs using (a) PEDOT:PSS and (b) *p*-pTFF-C₂F₅SIS as HILs.

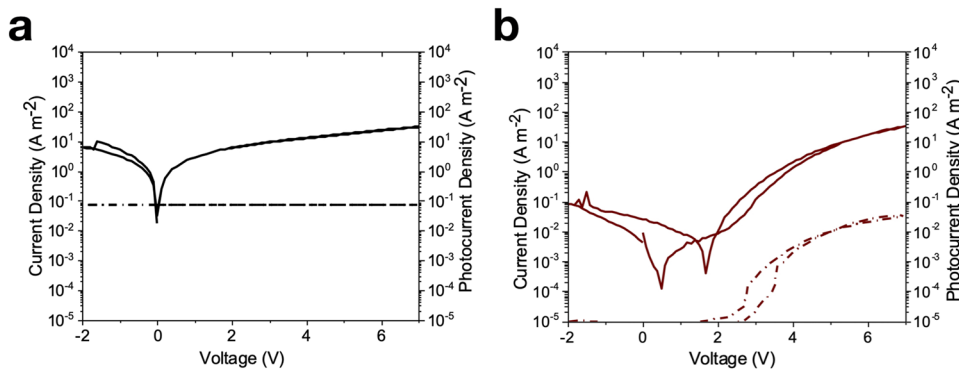


FIG. 5. Current density–voltage and luminance characteristics of PePoLEDs with (a) PEDOT:PSS (1 day aging) and (b) with *p*-pTFF- C_2F_5 SIS (21 days aging).

both types of devices (Fig. 5) remained unchanged. However, the PEDOT:PSS-based device exhibited a complete loss of light output after only 1 day of storage in nitrogen [Fig. 5(a)]. In contrast, the *p*-pTFF- C_2F_5 SIS-based device remained stable for a period over 21 days [Fig. 5(b)]. We ascribed the significant deterioration of the devices with PEDOT:PSS to the hygroscopicity of the HIL,²⁷ which would inevitably harm the lifetime of the adjacent perovskite film.

In conclusion, we described a general strategy to improve the device performance of LEDs based on perovskite:polymer blends using a heavily doped, solution-processed polymer hole-injection layer *p*-pTFF- C_2F_5 SIS. Preliminary results showed that the integration of this HIL in PePoLEDs led to working and stable devices, whereas devices with PEDOT:PSS exhibited high leakage currents and unstable behavior over time. The strongly reduced leakage current enables determination of the hole transport properties of the perovskite:polymer blend. The power-law dependence of the current density on the voltage is a characteristic for trap-limited currents with traps that are distributed in energy.

See the [supplementary material](#) for the experimental session and additional data.

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