Inverted planar perovskite solar cells are of considerable interest since the discovery of bipolar transport properties in perovskites and the report on the perovskite/fullerene planar heterojunction structure in 2013. Compared to titanium dioxide (TiO₂) based planar perovskite solar cells that usually require high-temperature (>450 °C) treatment, inverted perovskite solar cells are more compatible with facile solution processing techniques used for producing organic solar cells. Optimization of perovskite film morphology on poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) coated substrates has enabled inverted perovskite solar cells to achieve power conversion efficiencies (PCEs) approaching the record values obtained by their TiO₂-based counterparts. Particularly, inverted perovskite/fullerene planar heterojunction solar cells effectively eliminate or suppress photocurrent hysteresis associated with perovskites.

In an inverted architecture, the perovskite film is deposited on top of a hole extraction layer (HEL), typically PEDOT:PSS. However, the acidity of PEDOT:PSS is often detrimental to device performance and stability. Several solution processable inorganic substitutes for PEDOT:PSS, such as vanadium oxide (V₂O₅), nickel oxide (NiOₓ), and copper iodide (CuI), have been examined as HEIs in inverted perovskite solar cells; unfortunately, their processing methods are more complicated and less environmentally friendly than PEDOT:PSS cast from aqueous solutions. To maximize device efficiency, high-temperature annealing is required for V₂O₅ (500 °C), NiOₓ (300 °C), and CuI cast from volatile organic solvents such as acetonitrile. Hence, novel organic HEIs have emerged as promising alternatives to PEDOT:PSS in particular polyelectrolytes due to their wettability by the perovskite precursor solution. For example, Choi et al. reported a water/methanol-processed polyelectrolyte as a hole extraction material in inverted perovskite solar cells, affording a maximum PCE of 12.5%, while Li et al. developed a water soluble polyelectrolyte for inverted perovskite solar cells that required thermal annealing at 140 °C for 30 min to achieve a maximum PCE of 16.6%.

To efficiently extract holes from perovskite active layer and generate large built-in potential (V₉₀) across the devices, we sought a material that possesses relatively high work function (W) and simplifies the preparation of high-quality perovskite layers. Recently, we found that poly(arylene-vinylene) (PAVs) with polar side chains can be synthesized by the Horner–Wadsworth–Emmons coupling/polymerization in water without using toxic reagents/catalysts. This method provides an avenue to produce PAVs with a broad backbone modification, especially to facilitate the introduction of electron-deficient monomers into the polymer backbone, which lowers the highest occupied molecular orbital (HOMO) energy level of the resulting conjugated polymer and thus increases the work function of the material. Also, this new method provides a route to fabricate PAVs with reasonably high molecular weight and a high degree of trans-vinylene linkages that promote planarization of the polymer backbone by removing torsional interactions between aryl-rings, thus extending conjugation. Here, we show that a PAV-based conjugated polyelectrolyte (PVBT-SO₃⁻)

Figure 1a) developed through this polymerization strategy can be used as a hole extraction material for efficient inverted perovskite solar cells that can be cast from aqueous solutions and used without thermal annealing.

Fullerene/perovskite planar heterojunction solar cells, shown in Figure 1a, were fabricated by a one-step deposition process starting from indium tin oxide (ITO) substrates (hole extracting electrode). Aqueous solutions of PEDOT:PSS or PVBT-SO₃⁻ were spin-coated onto ITO substrates to serve as the HEL. PVBT-SO₃⁻ formed uniform films on ITO substrates, even for films 5 nm in thickness, with no aggregation observable by optical microscopy (Figure S1, Supporting Information). The perovskite precursor solution (Pb(OAc)₂ and methylammonium iodide (MAI)) was spin-coated onto an ITO/HEL substrate, followed by mild thermal annealing (at 90 °C for 5 min) to form the photoactive layer. As shown in Figure 1b,c, uniform and continuous perovskite films formed on the ITO/HEL substrates. Notably, perovskite films on ITO/PVBT-SO₃⁻ substrate had larger crystallites (crystal size ≈200 nm) and were free of pinholes when compared to films on ITO/PEDOT:PSS substrates. Powder X-ray diffraction (Figure S2, Supporting Information) showed...
peaks attributable to (100), (111), (200), and (220) planes of the tetragonal phase of the perovskite on both glass/PEDOT:PSS and glass/PVBT-SO₃ substrates. To facilitate selective electron extraction from the perovskite, phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) was spin-coated onto the perovskite layer from chlorobenzene. This was followed by spin-coating an interface modification layer of C₆₀-N[46] (Figure S3, Supporting Information) from 2,2,2-trifluoroethanol (TFE). Silver electrodes were then thermally evaporated onto the C₆₀-N layer for electron extraction as shown in Figure 1a.

As shown in Figure 2a, devices utilizing the conventional PEDOT:PSS HEL gave a maximum PCE of 12.6% with an open circuit voltage ($V_{OC}$) of 0.89 V, a short circuit current density ($J_{SC}$) of 19.6 mA cm$^{-2}$, and a fill factor (FF) of 72.0%. This PCE is comparable to that reported by Bolink and co-workers using the same perovskite precursor and mild thermal treatment (90°C for 5 min).[47] For devices with a PVBT-SO₃ HEL, the influence of the HEL thickness was probed. Devices with a thin HEL (5 nm) show a slightly higher $J_{SC}$, but a relatively lower FF, while with a thickness of 20 nm, both the $J_{SC}$ and FF of the devices decrease (see Figure S4 and Table S1, Supporting Information). Space charge limited current measurements yielded a hole mobility of $2.67 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ for PVBT-SO₃ (Figure S5, Supporting Information), which may not provide sufficient hole transport for the thicker films (20 nm). Hence, we found 10 nm to be an optimum thickness for the PVBT-SO₃ HEL. Devices with a thin HEL (5 nm) show a slightly higher $J_{SC}$, but a relatively lower FF, while with a thickness of 20 nm, both the $J_{SC}$ and FF of the devices decrease (see Figure S4 and Table S1, Supporting Information). Space charge limited current measurements yielded a hole mobility of $2.67 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ for PVBT-SO₃ (Figure S5, Supporting Information), which may not provide sufficient hole transport for the thicker films (20 nm). Hence, we found 10 nm to be an optimum thickness for the PVBT-SO₃ HEL. The use of PVBT-SO₃ as the HEL (10 nm) afforded a maximum PCE of 15.9% with a $V_{OC}$ of 0.97 V, a $J_{SC}$ of 21.2 mA cm$^{-2}$, and a FF of 77.4%. Thus, PCEs achieved by the as-spun PVBT-SO₃ layer are 26% higher than the device based on PEDOT:PSS (where the HEL required more extensive thermal annealing). Notably, the PVBT-SO₃ containing devices show significantly less hysteresis than devices with PEDOT:PSS layers. External quantum efficiency (EQE) measurements shown in Figure 2b confirm the improved $J_{SC}$ of the devices employing PVBT-SO₃ as the HEL. We performed steady-state measurements for the two best performing devices containing either PEDOT:PSS or PVBT-SO₃ (Figure 2c). Under simulated AM1.5G radiation (100 mW cm$^{-2}$) and bias voltage at the maximum power point, the PVBT-SO₃ based device produced a more stable output current than the PEDOT:PSS based device, with the latter showing a diminished current over time. Long-term air stability was tested by storing five separate devices of each type (PEDOT:PSS and PVBT-SO₃) in the absence of light (Figure 2d), then returning the devices to the glovebox for testing. Over 10 h storage, the PVBT-SO₃ devices showed no degradation, while the average PCE of PEDOT:PSS devices decreased by ~20%. During the first ~40 h, the PEDOT:PSS devices degraded slightly faster than PVBT-SO₃ devices. However, after ~40 h, the PEDOT:PSS devices degraded rapidly, with the average PCE decreasing by 70% after ~90 h of storage. In contrast, the average PCE for the PVBT-SO₃ devices decreased by only ~20% during the same timeframe. Since the acidity of PEDOT:PSS is detrimental to long-term device performance and stability,[43] the pH neutrality (provided in Figure S6, Supporting Information) of PVBT-SO₃ may assist with the improved device stability. To test the reproducibility, 80 devices of each type were fabricated and tested, as shown in Figure 2e,f and Figures S7 and S8 (Supporting Information). The PEDOT:PSS devices afforded an average PCE of ~11%, while PVBT-SO₃ based devices gave an average PCE of ~14%, attesting to the reliable and reproducible device performance improvement when using PVBT-SO₃ as the HEL.

Electrochemical impedance spectroscopy (EIS) measurements were performed to understand the recombination losses...
and charge transport properties in devices with different HELs. In the EIS measurement, a small applied AC voltage (20 mV) measures device impedance as a function of frequency ($\omega$), sweeping from 100 Hz to 1 MHz under simulated AM1.5G irradiation (100 mW cm$^{-2}$) inside an N$_2$-filled glovebox. As shown in Figure 3a, the Nyquist plot for each device type shows two semicircles associated with different time constants ($\tau$), representing two distinct charge transport regimes. The semicircle closest to the origin, associated with the higher frequency spectrum, is attributed to impedance arising predominantly from the electronic transport and recombination kinetics. The second semicircle, associated with the low frequency regime, is attributed to the impedance from slow relaxation/diffusion of ions. At 0 V applied DC bias, the first semicircle (high-frequency region) of the Nyquist plot is associated with the recombination resistance ($R_{\text{rec}}$). The PVBT-SO$_3$ containing devices show higher $R_{\text{rec}}$ values compared to PEDOT:PSS containing devices, as shown in Figure 3a, which corresponds to
a reduced recombination loss and correlates with the superior device performance observed when using PVBT-SO$_3$. Shown in Figure 3b are Mott–Schottky (MS) plots for each type of devices obtained by EIS characterization. The interfacial charge density is inversely proportional to the slope of the MS plot assuming an equivalent dielectric constant for both devices.\footnote{A steeper slope was found for PVBT-SO$_3$ containing devices (−1.0 × 10$^{13}$) relative to PEDOT:PSS containing devices (−9.4 × 10$^{10}$), indicating a lower interfacial charge density for the PVBT-SO$_3$ case by over two orders of magnitude, and thus more efficient charge extraction for PVBT-SO$_3$. Therefore, PVBT-SO$_3$ acts as a more efficient HEL relative to PEDOT:PSS, due to reduced recombination losses and interfacial charge density within the devices.}

Time-resolved photoluminescence (TRPL) measurements were performed on perovskite/HEL samples to assess the efficiency of charge separation in the PVBT-SO$_3$ versus PEDOT:PSS samples. Figure 4a–c shows PL images obtained from identically prepared perovskite films on a) clean glass, b) glass/PEDOT:PSS, and c) glass/PVBT-SO$_3$. The three images show a similar polycrystalline structure of the luminescent perovskite film, but the PL is strongly quenched in the presence of the PVBT-SO$_3$ HEL. This effect is seen clearly in Figure 4d, showing that the perovskite spectra are similar for the different samples but generate only ≈1/20 the PL intensity. Figure 4e shows representative PL decay traces from the three different perovskite samples. Interestingly, the presence of the HEL perturbs the fluorescence decay rate only slightly; single-exponential fits to the PL decay provide decay constants of 0.034 and 0.029 ns$^{-1}$ for the PEDOT:PSS and PVBT-SO$_3$ interlayers, respectively. This counterintuitive result can be understood by considering that the PL emission in perovskites does not typically arise from a simple radiative decay of optically generated excitons. Kamat and co-workers\footnote{A steeper slope was found for PVBT-SO$_3$ containing devices (−1.0 × 10$^{13}$) relative to PEDOT:PSS containing devices (−9.4 × 10$^{10}$), indicating a lower interfacial charge density for the PVBT-SO$_3$ case by over two orders of magnitude, and thus more efficient charge extraction for PVBT-SO$_3$. Therefore, PVBT-SO$_3$ acts as a more efficient HEL relative to PEDOT:PSS, due to reduced recombination losses and interfacial charge density within the devices.} showed that excitons in perovskites undergo dissociation into free carriers on a time scale of a few picoseconds; the PL emission on longer timescales arises from exciton regeneration from mobile carriers. The HEL decreases local hole concentration by extraction, thus decreasing PL intensity without significantly affecting PL decay rate. Thus the combined wavelength and time-resolved PL measurements support the EIS and other measurements that the PVBT-SO$_3$ interlayer acts as an efficient charge extractor, reducing the perovskite PL intensity by efficient extraction of holes into the interlayer.

Kelvin probe force microscopy (KPFM) was used to evaluate the work function (W) of different architectures with
PEDOT:PSS or PVBT-SO$_3$ (Figure 5). We use the relationship: $q \cdot V_{\text{CPD}} = (W_{\text{probe}} - W_{\text{sample}})$ to calculate W from measured contact potential differences between the sample and the probe ($V_{\text{CPD}}$). HELs were introduced by spin-coating onto Au-coated Si substrates, and KPFM measurements were conducted. Tapping mode atomic force microscopy (AFM) images for PEDOT:PSS and PVBT-SO$_3$ were shown in Figure 5a,b, respectively. Color mode AFM images, overlaid on height images, for PEDOT:PSS and PVBT-SO$_3$ films have a comparable roughness, as indicated by tapping mode AFM. Consequently, the difference in W is attributed to the electronic properties of the polymer. Ultraviolet photoelectron spectroscopy was used to determine the ionization potential (IP) from the low-binding energy onset. The IP of PVBT-SO$_3$ was found to be 5.19 eV, which corresponds to the HOMO level of the polymer.$^{[45]}$ Since the HOMO level of PEDOT:PSS is $\approx$5.0 eV$^{[51,52]}$ the deeper HOMO level of PVBT-SO$_3$ (5.19 eV) contributes to the higher work function of the bulk film. Since all devices contain exactly the same electron transport layer (ETL), the work function offset of the HEL and ETL determines the magnitude of the built-in-potential ($V_{\text{bi}}$) across the active layer. This $\approx$0.1 eV increase in W of PVBT-SO$_3$ film affords devices with a larger $V_{\text{bi}}$, which is crucial for solar cell devices with a higher $V_{\text{oc}}, J_{\text{sc}}$, and FF.$^{[53]}$ The deeper HOMO level of PVBT-SO$_3$ HEL may contribute to the improved $V_{\text{oc}}$ of the device.$^{[51,52,54]}$

In summary, a water-processable HEL that requires no thermal annealing was developed as an alternative to the widely used PEDOT:PSS for the fabrication of high performance inverted perovskite solar cells. A maximum PCE of 15.9% was achieved by using PVBT-SO$_3$ as the HEL, representing an $\approx$26% improvement over the PEDOT:PSS containing devices. PVBT-SO$_3$ based devices also showed substantially improved stability and long-term air stability. EIS measurements suggest that PVBT-SO$_3$ containing devices have larger recombination resistance and more efficient charge extraction relative to those with PEDOT:PSS. KPFM characterization confirms that PVBT-SO$_3$ films show higher work function than that of PEDOT:PSS, which provides a larger $V_{\text{bi}}$ in devices containing PVBT-SO$_3$ and thus a better performance, while time-resolved PL measurements further confirmed an efficient charge extraction of PVBT-SO$_3$ interlayers from perovskite. The results presented here for PVBT-SO$_3$ as a new hole extraction material to improve solution processed perovskite solar cells indicates conjugated polyelectrolytes may possess superior charge extraction properties and their modification on electrodes is an additional advantage for generating large $V_{\text{oc}}$ across the devices, which will encourage the design and utility of new polymers that advance photovoltaic technology.

**Experimental Section**

**Materials:** PVBT-SO$_3$ and C$_{60}$:N were synthesized according to published procedures.$^{[45,46]}$ Pb(OAc)$_2$ was used as received from Sigma-Aldrich. MAI was received from 1-Material. PC$_{61}$BM was purchased from Nano-C. All the solvents used in this work were purchased from Sigma-Aldrich.

**Device Fabrication:** The ITO-coated glass substrates (20 $\pm$ 5 $\Omega$ per square) were obtained from Thin Film Devices Inc., and were cleaned through ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol and then dried in an oven for 6 h. PEDOT:PSS (H.C. Starck, I 4083) was spun-coated on precleaned ITO substrates at 3500 rpm for 40 s and annealed at 150°C for 30 min. PVBT-SO$_3$ water solution (2 mg mL$^{-1}$) was spin-coated onto precleaned ITO substrates at 3000 rpm for 40 s and annealed at 150°C for 30 min. PVBT-SO$_3$ water solution (2 mg mL$^{-1}$) was spin-coated onto precleaned ITO substrates at 4000 rpm for 40 s without any post-treatment. The film thicknesses of PEDOT:PSS and PVBT-SO$_3$ are $\approx$30 nm and $\approx$10 nm as confirmed by the profilometer. The perovskite layer was formed by spin-coating a solution of Pb(OAc)$_2$ and MAI (1:3 molar ratio) in N,N-dimethylformamide onto the HEL/ITO substrates at a spin-speed of 2000 rpm for 60 s inside a glove box (N$_2$ atmosphere, $<1$ ppm O$_2$, $<1$ ppm H$_2$O). As-cast films were then annealed in dark at 90°C for 3 min in a glove box. A thin layer of PC$_{61}$BM (60–70 nm) as electron transport layer was then spin-coated inside a glove box (N$_2$ atmosphere, $<1$ ppm O$_2$, $<1$ ppm H$_2$O) from a solution in chlorobenzene (20 mg mL$^{-1}$) at 1000 rpm for 60 s. C$_{60}$N in TFE (3 mg mL$^{-1}$) was spin-coated onto PC$_{61}$BM surface with a thickness of $\approx$10 nm. Finally, 100 nm Ag electrode was deposited (area 6 mm$^2$ defined by metal shadow mask) on the active layer under high vacuum (1 $\times$ 10$^{-6}$ mbar) using a thermal evaporator.
Device Characterization: Current density–voltage (J–V) characteristics were measured in an N₂ atmosphere (unless otherwise stated) using a Keithley 2400 source-meter under simulated AM1.5G irradiation using a 300 W Xe lamp solar simulator (Newport 91160). The light intensity was adjusted with an NREL-calibrated Si reference cell and KG-5 filter. The illuminated area (0.055 cm²) was defined by a metal photomask with an aperture and used in all reported PCE measurements. The QE-PV-SI Measurement Kit (Newport/Oriel Instruments) with 150 W Xe arc lamp, monochromator, and calibrated silicon reference cell with power meter are used for quantum efficiency (QE)/incident photon to charge carrier efficiency measurement for solar cells over a 400–1100 nm spectral range. EL was measured using an Agilent 4294A Precision Impedance Analyzer under 100 mW cm⁻² light intensity at 20 mV applied AC amplitude. DC bias voltage was kept at 0 V. Frequency was swept from 100 Hz to 1 MHz.

KPFM Measurements: Samples for KPFM were prepared on gold (Au) substrates. The preparation is exactly the same as that in device fabrication. KPFM measurements were made in air using an Asylum Research MFP3D-stand-alone AFM. The probes (ANSCM-PT) used were Pt/Ir coated (~25 nm) Si probes with a spring constant of 1–5 N m⁻¹ as supplied from AppNano. Scans were typically 5.0 µm × 1.25 µm (512 pixel × 128 pixel) at a scan speed of 0.5 Hz. The nap mode lift height (∆H) was 30 nm for all scans. The Au electrode was grounded for all measurements. Work function calibration was done using Au coated on SiO₂ substrates, and assuming the work function of gold is 5.1 eV.

Pl Measurements: PL spectra were obtained using 405 nm pulsed excitation and imaging onto an avalanche photodiode (ACTON 3160a imaging spectrograph; time-resolved PL was taken with a time-to-digital converter (~405 nm pulsed excitation, and imaging onto an avalanche photodiode). The illuminated area (0.055 cm²) was defined by a metal photomask with an aperture and used in all reported PCE measurements. The QE-PV-SI Measurement Kit (Newport/Oriel Instruments) with 150 W Xe arc lamp, monochromator, and calibrated silicon reference cell with power meter are used for quantum efficiency (QE)/incident photon to charge carrier efficiency measurement for solar cells over a 400–1100 nm spectral range. EL was measured using an Agilent 4294A Precision Impedance Analyzer under 100 mW cm⁻² light intensity at 20 mV applied AC amplitude. DC bias voltage was kept at 0 V. Frequency was swept from 100 Hz to 1 MHz.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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