Optimizing Lignosulfonic Acid-Grafted Polyaniline as a Hole-Transport Layer for Inverted CH₃NH₃PbI₃ Perovskite Solar Cells

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ABSTRACT: A conducting polymer of lignosulfonic acid-grafted, polyaniline-doped camphorsulfonic acid (LS-PANI-CSA), created via a low-temperature solution process, has been explored as an efficient hole-transport layer (HTL) for inverted single cation-anion CH₃NH₃PbI₃ perovskite solar cells. The performance of the solar cell was optimized in this study by tuning the morphology and work function of LS-PANI-CSA films using dimethylsulfoxide (DMSO) as a solvent in treatment. Results showed that DMSO washing enhanced the electronic properties of the LS-PANI-CSA film and increased its hydrophobicity, which is very important for perovskite growth. The perovskite active layer deposited onto the DMSO-treated LS-PANI-CSA layer had higher crystallinity with large grain sizes (>5 μm), more uniform and complete surface coverage, and very low pinhole density and PbI₂ residues compared to untreated LS-PANI-CSA. These enhancements result in higher device performance and stability. Using DMSO-treated LS-PANI-CSA as an HTL at 15 nm of thickness, a maximum 10.8% power conversion efficiency was obtained in ITO/LS-PANI-CSA/MAPbI₃:PCBM/BCP/Ag inverted-device configurations. This was a significant improvement compared to 5.18% for devices based on untreated LS-PANI-CSA and a slight improvement over PEDOT:PSS-based devices with 9.48%. Furthermore, the perovskite based on treated LS-PANI-CSA showed the higher stability compared to both untreated LS-PANI-CSA and PEDOT:PSS HTL-based devices.

INTRODUCTION

Due to its high efficiency, solution processability, and easy and low-cost fabrication, hybrid organic/inorganic perovskite is frequently investigated for use in thin-film solar cells. Perovskite has outstanding optoelectronic properties such as a long carrier diffusion length, broad light absorption throughout the visible wavelength region, and controllable band gap.1−3 The traditional mesoscopic perovskite architecture utilizes a high-temperature-processed mesoporous metal oxide scaffold (titanium oxide and zinc oxide) as the electron transport layer (ETL), which is incompatible for flexible and tandem solar cells. Moreover, the relatively high cost of 2,2′,7,7′-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9′-spirobifluorene (spiro-OMeTAD), which is used as the hole-transport layer (HTL) in the traditional mesoscopic architecture, has limited the practical development of perovskite solar cells. Therefore, it is important to find a new HTL for planar perovskite devices that has a suitable work function to make ohmic contacts with the perovskite active layer. Inverted-type planar architectures with low-temperature processing have emerged as an alternative to traditional mesoscopic architectures. Poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS) is often used as an HTL in both organic and perovskite solar cells. However, PEDOT:PSS has poor long-term stability due to its hygroscopic and acidic nature.4 In the case of inverted perovskite architecture, several inorganic p-type semiconductors have been used as HTLs to improve the device efficiency, such as CuSCN, CuO, Cu₂O, Cu-doped NiO, NiOₓ, CuS, CuOₓ, Mg-doped NiO, and CuI.9−19 However, small organic molecule-based HTLs have been developed for high-performance perovskite devices; they require an easier solution process, and their optical and electrochemical properties can be relatively easily tuned by changing certain functionalities.20−22 Moreover, most polymeric HTLs contain nitrogen and sulfur, which are electron-rich atoms that help improve the performance of a device.21,23

Thus, new low-temperature, solution-processed organic HTLs for perovskite-based solar cells are needed. Among various conducting polymers, polyaniline (PANI) is one of the
most intriguing conjugated polymers because of its tunable conductivity upon doping and simple low-cost method required to synthesize. PANI has been used as an alternative HTL in various electronic devices, including light-emitting diodes and organic and traditional mesoscopic perovskite solar cells. Alternative HTL-based PANI has shown high transmittance compared to PEDOT and high stability compared to PEDOT:PSS. Conventional PANI is limited by its processability, and it becomes insoluble in common organic solvents when doped with most acids. However, several methods have been used to improve its processability. PANI-doped poly(sodium 4-styrenesulfonate) (PANI:PSS) showed increased dispersion in water. However, some PANI:PSS composite particles have limited applications due to their lack of stability when dispersed in water; therefore, work has been done to improve dispersibility by modifying particle size.

Similar to the PANI:PSS, lignosulfonic acid-doped polyaniline (LS-PANI) has shown high polymer dispersion due to the solubility of the lignosulfonate counterion. Lignosulfonates are commercially available as sodium or ammonium salts, and the latter can be made into lignosulfonic acid simply by utilizing proton-exchange resins. An extremely water-soluble polymeric acid, lignosulfonic acid is able to be a template for polyaniline polymerization. Although LS-PANI exhibits good dispersibility in water and higher dispersibility in polar aprotic solvents such as N-methyl-2-pyrrolidone (NMP) or dimethylsulfoxide (DMSO), its conductivity is still low for some applications. Therefore, additional acid doping is needed to increase its conductivity. Additional LS-PANI acid doping increases the electron delocalization on the polyaniline backbone, leading to more chain–chain interaction and, thus, higher conductivity. The degree of protonation or “doping” in PANI can be adjusted by changing the molar ratio of the protonic acid to an imine nitrogen atom. It has been mentioned in the literature that increasing the acid doping level increases not only the conductivity but the work function of the PANI as well. The work function was 4.78 ± 0.13 eV at a full doping level because the high acid doping level of the polymer caused the Fermi level to increase toward the highest occupied molecular orbital. Spectroscopy showed that the PANI protonated by sulfonic acid had higher dispersibility and conductivity in m-cresol than those of other polar and nonpolar solvents. This is due to the expanded coil conformation of the protonated polymer chain, which leads to removal of the twist defects between aromatic rings and allows for a more extensive conjugation of the π orbitals. Therefore, m-cresol was not only a solvent but also a secondary dopant for protonated PANI because its strong interaction with the polymer chain led to increased molecular conformation from a compact coil to an extended coil.

In this work, LS-PANI was synthesized and employed for the first time as an HTL for an inverted planar CH₃NH₃PbI₃ perovskite device after protonation with camphorsulfonic acid. Camphorsulfonic acid (CSA) plays an important role in tuning the work function of the polymer to enable ohmic contact with the perovskite valance band. Therefore, fully protonated LS-PANI with CSA was processed, and the effect of film thickness...
on the device performance was examined. Additionally, the morphology and hydrophobicity of the LS-PANI-CSA films were studied, which are very important factors for the growth and stability of CH$_3$NH$_3$PbI$_3$ perovskite-based solar cells. It is known that perovskite film quality, including grain size, grain boundaries, and crystalline structure and orientation, can be controlled through preparation methods.\textsuperscript{43–45} Mixed antisolvents,\textsuperscript{46–48} or additive materials.\textsuperscript{49} Perovskite film quality is also influenced by the surface energy properties (e.g., solvent wettability) of the HTL/ETL underlayers.\textsuperscript{50} The morphology and optoelectronic properties of the perovskite active layer and HTL underneath are crucial to the resulting high-performance inverted-architecture device. Multiple characterization techniques, including X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), Kelvin probe force microscopy (KPFM) techniques, Raman spectroscopy, and UV–vis spectrometry, were implemented to investigate the processing and fabrication of the device layers.

## RESULTS AND DISCUSSION

### Structure and Morphology of the HTL and Active Layers of the Device

In the beginning of the study, several organic sulfonic acids were utilized as additional protonic acid dopants for LS-PANI, including p-toluenesulfonic acid (p-TSA), dodecylbenzenesulfonic acid (DBSA), and CSA. The LS-PANI films protonated by the three sulfonic acids were analyzed by AFM, and the results showed that the CSA produced the highest quality film with a lower surface roughness than that of p-TSA and DBSA films. The root mean square (RMS) of the LS-PANI-CSA surface was 3.39 nm, in contrast to 14.7 and 8.49 nm for the LS-PANI-p-TSA and LS-PANI-DBSA films, respectively (Figure S2). To further improve the quality of the LS-PANI-CSA films, three high-polarity solvents, NMP, dimethylformamide (DMF), and DMSO, were used to wash the films. NMP and DMF solvents removed some polymers from the surface, resulting in increased surface roughness (Figure S2), but DMSO produced a high-quality uniform film with lower surface roughness than that of the untreated pristine LS-PANI-CSA films. Throughout the article and in the figures, films may be referred to as UT-LS-PANI-CSA (untreated/no solvent treatment) or as T-LS-PANI-CSA (solvent treated).

In the AFM images of the UT-LS-PANI-CSA (Figure 1a) and DMSO-treated LS-PANI-CSA (Figure 1b), distinct agglomeration of polymer grains was visible in the pristine samples, while in the solvent-treated films, the accumulated polymer grains were diminished. The RMS of the DMSO-treated LS-PANI-CSA film at a 10 μm scan size was 1.23 nm, which is lower than the untreated LS-PANI-CSA film’s RMS of 4.87 nm. As can be seen in Figure 1a, the polymer grains, which have numerous features, were distributed over the surface, resulting in a nonuniform film with high roughness compared to the DMSO-treated film. Upon washing the samples, these features were removed, leading to a smoother surface, which become similar to those of the PEDOT:PSS morphology that has a 0.93 nm RMS (Figure 1c). Therefore, LS-PANI-CSA with and without DMSO solvent treatment was focused on as an HTL for an inverted perovskite device.

The XPS survey scans of pure LS-PANI and LS-PANI-CSA with and without DMSO washing are plotted in Figure S3a. The figure shows peaks at binding energies of 168.23, 284.99, 400.10, and 531.95 eV, which correspond to the four elements of interest: sulfur (S 2p), carbon (C 1s), nitrogen (N 1s), and oxygen (O 1s), respectively. The sulfur peak was only evident in protonated samples, disappearing in the unprotonated LS-PANI sample. Using DMSO as a washing solvent did not show any negative side effects on the LS-PANI-CSA materials with the four elemental peaks remaining the same after treatment. The S/N atomic and weight ratios were determined from XPS measurements of LS-PANI-CSA before and after DMSO washing, in addition to the pure LS-PANI films where the film was etched for 10 s by an ion beam. The S/N atomic ratio was reduced from ~0.5:1 to ~0.2:1 after DMSO treatment because it removed some big particles from the film’s surface, as confirmed by AFM, and reduced the m-cresol content from the film surface.

To investigate the influence of solvent treatment on the primary (CSA) and secondary (m-cresol) doping, UV–vis spectroscopic analysis was employed (Figure 1d). The untreated LS-PANI-CSA film showed the typical absorption spectrum of PANI where the polaron–π* transition is evident at approximately 450 nm and a delocalized π–π* band is evidenced by the free-carrier tail rising at wavelengths of >800 nm.\textsuperscript{37,38,39} The UV–vis transmittance spectra of treated LS-PANI-CSA films showed lower transmittance, specifically at wavelength intervals between 550 and 750 nm, than that of the spectra of the pristine film. As can be seen in Figure 1d, after DMSO treatment, peaks at 330 and 740 nm, associated with π–π* and localized π–π* bands, respectively, were present in the spectrum, which indicates the removal of the dopant (e.g., CSA) and two residues of m-cresol solvent by the treatment process. Even though the treatment process reduced the transmittance spectra of the polymer, the 15 nm treated films showed good transparency in the visible region from a maximum (94.2%T) wavelength of 504 nm to a minimum (89.2%T) of 692 nm. While both treated and untreated LS-PANI-CSA films had lower transmittance than that of ITO (shown as reference in Figure 1c), the HTLs of interest in this study can still be considered a good window to allow the visible spectrum to reach the active layer. UV–vis analysis proved that the LS-PANI-CSA chains kept some expanded coil formation due to the existence of a free carrier tail after the treatment process. The transmittance spectra of untreated LS-PANI-CSA showed lower transparency than that of the PEDOT:PSS film at the interval wavelength from 600 nm toward the ultraviolet region and higher transparency from 600 nm toward the infrared region, while treated LS-PANI-CSA showed lower transparency than that of PEDOT:PSS over much of the spectral region of interest.

The Raman spectra of 15 nm-thick untreated and DMSO-treated LS-PANI-CSA films were recorded using a 632.8 nm laser to further examine structural changes. Results indicated that the treated LS-PANI-CSA film (Figure 1e) peaks shifted, and peak intensities were reduced for the C–N quinoid ring (~1337 cm$^{-1}$) and delocalized polaron vibrations (~1383 and ~1642 cm$^{-1}$) in the extended polymeric conformation. A small shift of the primary quinoid rings’ C=H occurred at 1168 cm$^{-1}$ in treated LS-PANI-CSA, compared to 1178 cm$^{-1}$ in untreated LS-PANI-CSA; this shift is attributed to the same mode in the benzoid segments.\textsuperscript{33} Furthermore, the band at 1465 cm$^{-1}$, assigned to the C==C stretching vibration of the quinoid ring, was strong in the DMSO-treated film spectra but not as evident in the untreated film, which likely still had m-cresol on the surface. These changes can be attributed to the polymer
having a more quinoid-like character and, as was stated in the section on UV−vis, the removal of the dopant (e.g., CSA) and residual m-cresol solvent by treatment.

Because the HTL influences the deposition and growth of perovskite in inverted device architectures, we characterized the perovskite layer after deposition on the untreated and treated LS-PANI-CSA HTLs. Top-view SEM images (Figure 2a−c) of perovskite films deposited on the HTLs make it clear that the HTLs influenced the perovskite films. The perovskite film had large grain sizes when deposited onto treated LS-PANI-CSA, reaching ~5 μm (and low variation in sizes), whereas, when deposited onto the untreated LS-PANI-CSA film, the grains were less than 1 μm (with random variation) and some unclear grain sizes were observed (Figure S4). The grain boundaries of perovskite deposited onto the untreated and PEDOT:PSS films were not perpendicular to the substrate due to the polymer's low hydrophobicity leading to unclear grain boundaries of perovskite films. Furthermore, untreated LS-PANI-CSA exhibited higher surface roughness (Figure 1a), which facilitates nucleation in small cavities, thus limiting the grain boundary mobility of the perovskite. The increased coverage and smoothness of the perovskite film on the solvent-washed LS-PANI-CSA suggests that DMSO treatment can induce homogenous nucleation by modifying the perovskite/HTL interfacial energy, which, in turn, allows the perovskite crystals to grow evenly and have optimal contact with the LS-PANI-CSA surface. Additionally, the perovskite film becomes a darker black and shiny when deposited on the treated LS-PANI-CSA, which indicates good crystalline orientation. The larger grain size compared to the film thicknesses (a 6-fold difference) will greatly enhance the charge extraction process since the photogenerated charges would not need to go through a prohibitive amount of grain boundaries before being collected by the electrodes.

The contact angles of water on these polymers are shown in Figure 2d−f. As can be seen, LS-PANI-CSA after DMSO treatment had a larger contact angle of 80 ± 2° than that of the untreated LS-PANI-CSA (50 ± 2°) and PEDOT:PSS (30 ± 4°) due to the lower acidity (i.e., surface energy) of the treated surface. These results confirm that treated LS-PANI-CSA is more resistant to wetting than untreated and PEDOT:PSS films. Increasing the hydrophobicity of the polymer reduces the surface tension and, hence, the dragging force when the perovskite precursor is used; this allows for growth of larger grain boundaries than those on the untreated polymer surface. As can be seen in Video S1, the treated LS-PANI-CSA film was highly wettable by the perovskite precursor solution (mixture of 4:1 v/v of DMF:DMSO) compared to the untreated film shown in Video S2; this allowed the solution to spread rapidly on the polymer surface and lead to a uniform
perovskite layer with better coverage over the HTL. The increased hydrophobicity of LS-PANI-CSA after DMSO washing was also considered evidence of surface modification because it indicates reduced acidity of the dopant/m-cresol on the film surface.50,55

Surface energy studies complement findings from X-ray diffraction patterns (Figure 2g) that were sharper and more intense for perovskite films on the treated LS-PANI-CSA HTLs. The XRD patterns were recorded for MAPbI3 films deposited onto the glass/ITO/untreated LS-PANI-CSA and glass/ITO/treated LS-PANI-CSA substrates in ambient conditions at room temperature and 23−25% relative humidity. The films were annealed at 100 °C for 10 min, and the patterns are shown in Figure 2e. Strong peaks at 14.05°, 19.95°, 23.51°, 24.56°, 28.48°, 30.99°, 31.94°, 40.47°, 42.51°, and 43.24° are visible, which correspond to the reflections from the 110, 112, 211, 202, 310, 312, 224, 411, and 330 planes, respectively. This finding indicates that the perovskite layers produced from the cosolvents DMF and DMSO had highly crystalline (tetragonal) structures and no impurity peaks.56−61 Using the cosolvent approach, DMSO functioned both as a solvent and as a coordination reagent because it has a stronger ability to coordinate with PbI2 than that of DMF, while DMF only functions as a solvent, with a relatively higher evaporation rate than that of DMSO.62 Furthermore, forming a PbI2−MAI−DMSO intermediate-phase film hampered the fast reaction between PbI2 and MAI during the DMF evaporation.59 It has been reported that using only DMF as a solvent for the precursor solution results in additional peaks of unreacted PbI2 at 12.99° and 38.98°, even when the films are annealed at 100 °C. This residual PbI2 would reduce the performance of the devices due to its poor light absorption.59,62 The grain size of the perovskite was estimated using the Scherrer equation;63 the average crystallite sizes were approximately 44, 35, and 37 nm for perovskite deposited onto treated and untreated LS-PANI-CSA and PEDOT:PSS, respectively. As displayed in Figure 2g, the strong and narrow peak width confirmed that perovskite films exhibit better orientation on the treated LS-PANI-CSA surface than on the untreated or PEDOT:PSS surfaces. According to the literature, the binding energies of the elements in perovskite can shift depending on the ETL/HTL that the perovskite layer is deposited on and on the thickness of the active layer.64−66 Therefore, the XPS survey spectra were recorded for MAPbI3 deposited onto treated and untreated LS-PANI-CSA and PEDOT:PSS layers to identify all elemental species present in the composition of the MAPbI3 film. Figure S3b shows the XPS spectra of MAPbI3 perovskite films deposited onto LS-PANI-CSA with or without solvent treatment and PEDOT:PSS films. The electron photoemission peaks of the elements O (1s), N (1s), and C (1s) are located at binding energies ca. 532, 402, and 285 eV, respectively, while the doublet peaks of I (3d) and Pb (4f) elements with their associated spin−orbit splitting are located at around 619 and 138 eV, respectively. The elemental composition of both untreated and treated samples was mostly similar with no significant shifts in binding energies. Moreover, the results showed no other obvious elements in the sample other than those associated with the perovskite.

In order to evaluate the generation of charge carriers in the active layer over the untreated and treated HTLs, optical absorption coefficients (α) of the perovskite films were
estimated. Using the absorption spectrum (A), optical absorption coefficients (α) can be derived as
\[ \alpha = A \ln 10/L \]
where L is the sample thickness.\(^{67}\) Compared to perovskite deposited on untreated LS-PANI-CSA and PEDOT:PSS, the perovskite films deposited on treated LS-PANI-CSA had higher absorption coefficients along all the wavelengths except at absorption edges where perovskite films had a sharp discontinuity in decreasing of the absorption coefficients at absorption edges. It is clear from Figure 2h that the absorption coefficient of perovskite becomes lower after the wavelength of 580 nm until the absorption edge when perovskite is deposited onto the PEDOT:PSS layer. Furthermore, the energy band gap \(E_g\) was estimated using the power law of Tauc:\(^{68}\)

\[ hv = B (hv - E_g)^2 \]

where B is a constant related to the electrical conductivity and the energy level separation, \(q\), depends on the type of electronic transition. Theoretically, \(q\) equals 1/2 or 2 for a direct or indirect allowed transition, respectively.\(^{69,70}\) For direct allowed transition, the band gap of the MAPbI\(_3\) thin film deposited on treated and untreated ITO/LS-PANI-CSA was 1.567 eV, approximately the same for the deposited perovskite onto treated and untreated LS-PANI-CSA films (Figure 2i). This result is close to the theoretical value of 1.55 eV that was reported by Baikie.\(^{71}\) The deposition of perovskite onto treated LS-PANI-CSA without tuning the perovskite band gap\(^{72}\) is evidence that a high-quality, uniform, superior crystalline perovskite film leads to increasing the absorption coefficients.\(^{46,73,74}\)

**Electronic Properties of the Device Interface Layers.**

XPS was used to further analyze the untreated and treated LS-PANI-CSA surfaces without etching (as would be done in the KPFM measurement). The results demonstrate that the films treated with DMSO have a lower S/N ratio, approximately half, with no deviation compared to the untreated films, which have the higher S/N ratio with higher deviation, especially at 10 and 20 nm thicknesses, as shown in Figure 3a. As discussed earlier, the treated samples exhibit optical absorption and Raman spectra that is consistent with slight dedoping of the polymer backbone. Therefore, the conductivity and mobilities were investigated using I–V curves and a space charge-limited model (Figures S5 and S6) to determine the effect of treatment on electronic properties. The treated LS-PANI-CSA had similar conductivity and mobility to that of the untreated samples at the same film thickness (Figure 3b,c).

This finding is quite unexpected as conductivity is known to decrease with the doping level and may be attributed to other modifications to the electronic properties, such as work function. A film of PEDOT:PSS at 34 nm of thickness exhibited a conductivity and mobility similar to those of the 10 nm LS-PANI-CSA films.

In order to assess the efficiency of the charge transfer process, we performed work function (WF) analysis using Kelvin probe force microscopy (KPFM) on the transport layers of our device. Height and surface potential images of the treated and untreated LS-PANI-CSA films at three different thicknesses are shown in Figures S8 and S9. Potential histograms were fitted with Gaussian curves to find the mean value of the contact potential difference (CPD) for the sample; this is a good method to find the mean CPD with high accuracy.\(^{75}\) Between the treated and untreated samples, the change in the CPD was more than 131 mV, while it was less than 20 mV at different thicknesses of the same material, as shown in Figures S8 and S9. The slight deviation in the CPD in four different spots on the same samples might be attributed to the sample’s contamination, solvent residuum, or tip wearing; otherwise, surface roughness is the main reason for this deviation, which was observed in the mirror topology.\(^{75–80}\) To avoid issues in CPD measurement due to surface contamination or tip wear, the CPD measurement procedure was repeated many times using new tips and freshly prepared samples. The results consistently showed the same behavior, indicating that the deviation in the CPD might be due to the morphology or S/N atomic ratio of the surface films. On the other hand, the PEDOT:PSS sample showed a lower CPD with an average value of 54 mV compared to treated and untreated LS-PANI-CSA (Figure S10a), while unprotonated LS-PANI samples showed the higher CPD compared to treated and untreated protonated LS-PANI-CSA due to the lack of extra doping of the polymer by camphorsulfonic acid (Figure S10b). The KPFM results of the CPD and roughness for all samples are plotted in Figure 3d,e, respectively. It is clear from Figure 3b that the lower thickness results in a wider range of surface roughness before solvent treatment, which also increases the deviation in the CPD, but it can be overcome by solvent treatment. Without extra doping, the films are rougher and have a higher CPD. To convert the measured CPD of the samples to the absolute surface work function, eq S2 (found in the Supporting
Information) can be modified in case of tip routing as follows: \[ \Theta = \Theta_{\text{Sample}} = 4.6 \text{ eV} + \text{CPD}_{\text{HSOG}} - \text{CPD}_{\text{Sample}} \] (2)

Using eq 2, the absolute WF values were plotted (Figure 3f). The WF shifted at a specific thickness due to the variation in the roughness of that film.\(^{78-80}\) As has been reported in the literature, as surface roughness features grow smaller, the electron binding by the surrounding atoms gets weaker; therefore, the electrons are more able to escape from the surface, which leads to a lower WF. Likewise, when the surface roughness is reduced and the topography peaks become smoother, the surface electrons become more bound by the surrounding atoms, making it less easy for them to escape and, thus, increasing the WF of the surface.\(^{79,80}\)

It is clear from Figure 3 that the 15 nm-thick film showed the lowest roughness and highest WF of \(-4.86 \text{ eV}\) compared to the other thicknesses of LS-PANI-CSA films, while PEDOT:PSS showed lower roughness with a slightly higher WF of \(-4.88 \text{ eV}\) compared to all other investigated HTLs. As mentioned earlier, the solvent-treated film had a highly uniform surface with low roughness because the agglomerated LS-PANI-CSA had been removed. Moreover, the CPD of the ITO glass substrate, which is used here as the device anode, was measured and averaged for four different spots, resulting in an average CPD of 274.25 mV (Figure S8c) and a WF of \(-4.66 \text{ eV}\). The ITO WF results were in excellent agreement with previous reports.\(^{82}\)

Device Performance and Stability. An inverted perovskite photovoltaic (PV) device based on the structure depicted in Figure 4a, an indium-tin oxide (ITO)/LS-PANI-CSA with...
Photovoltaic Parameters Taken from the J–V Measurements of the Best Performing Device under Standard AM 1.5 Illumination (100 mW cm\(^{-2}\)) for Treated (T-) LS-PANI-CSA HTLs at Different Thicknesses

| HTLs              | scan direction | EQE\(^\text{a}\) | J–V   | \(V_{OC}\) (V) | FF (%) | PCE (%) | \(R_s\) (\(\Omega \text{cm}^2\)) |
|-------------------|----------------|-----------------|-------|----------------|--------|---------|-----------------|
| T-LS-PANI-CSA (10 nm) | forward        | 16.44           | 18.7  | 0.60           | 68     | 7.62    | 0.95            |
|                   | reverse         | 18.4            | 19.4  | 0.60           | 73     | 8.05    |                 |
| T-LS-PANI-CSA (15 nm) | forward        | 17.21           | 19    | 0.816          | 68     | 10.54   | 0.83            |
|                   | reverse         | 19.5            | 0.816 | 68             | 10.82  |         |                 |
| T-LS-PANI-CSA (20 nm) | forward        | 15.19           | 16    | 0.536          | 65     | 5.57    | 1.287           |
|                   | reverse         | 15.9            | 0.572 | 65             | 5.90   |         |                 |
| PEDOT:PSS (control device) | forward        | 18.1            | 0.860 | 57             |        | 8.87    | 182             |
|                   | reverse         | 18.83           | 0.864 | 61             | 9.48   |         |                 |

\(^{a}\)Estimated based on equation found in ref 92.

Table 1. Photovoltaic Performance Parameters Taken from the J–V Measurements of the Best Performing Device under Standard AM 1.5 Illumination (100 mW cm\(^{-2}\)) for Treated (T-) LS-PANI-CSA HTLs at Different Thicknesses

and without solvent treatment or PEDOT:PSS/MAPI\(_3/\)phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM)/bathocuproine (BCP)/Ag, was fabricated. The device architecture of the solar cell is illustrated in Figure 4b, and the energy level values of perovskite, BCP\(_3/\) and PCBM considered according to Troughton et al.\(^{87}\) and measured WF of the device layer are illustrated in Figure 4c. The device substrate has six individual cells, each with an individual 2.56 mm\(^2\) active area. The fabrication processes were the same except for the HTLs in which three groups of perovskite solar cells based on untreated and DMSO-treated LS-PANI-CSA at different thickness were compared with each other and with the performance and stability of the PEDOT:PSS perovskite-based device. To investigate the influence of LS-PANI-CSA thickness on device performance, three different thicknesses (10, 15, and 20 nm) of treated and untreated LS-PANI-CSA were tested. The AFM tapping mode was used to measure the thickness of films (Figures S11 and S12). Using the SEM cross section, the thicknesses of all device layers are shown in Figure S13. The current density–voltage (\(J–V\)) curves are shown in Figure 5, and the performance parameters derived from the \(J–V\) curves, including a forward and reverse scan direction of power conversion efficiency (PCE), short-circuit current density \(J_{sc}\), open-circuit voltage \(V_{oc}\), and fill factor (FF), are summarized in Table 1 for treated LS-PANI-CSA; the device performance for untreated LS-PANI-CSA is summarized in Table S1.

When LS-PANI-CSA was treated with DMSO, we observed a significant increase in its photovoltaic performance, mainly due to the formation of a more uniform and pinhole-free perovskite layer with large grains (Figure 2b). Moreover, the KPFM study showed that the untreated LS-PANI-CSA had a lower work function, even with full protonation by CSA (Figure 3d). Increasing the WF of LS-PANI-CSA from \(-4.74\) to \(-4.86\) eV after DMSO treatment at the HTL/perovskite interface resulted in a better energy alignment between the ITO and perovskite layer compared to thinner (\(~10\) nm) or thicker (\(~20\) nm) HTLs. Moreover, it was noted that reducing the film’s thickness to less than 10 nm did not allow enough coverage of the ITO/glass substrate by the perovskite, and many spots of ITO were clearly visible via AFM after solvent treatment.

A reduction of the LS-PANI-CSA thickness to 10 nm improved the device FF up to 73%. However, the conductivity and mobility of the polymer decreased at \(~10\) nm of thickness, leading to poorer device performance. Increasing the LS-PANI-CSA thickness up to 20 nm reduced all the key parameters of the perovskite device, raising the hysteresis in the \(J–V\) curves (Figure 5c). All the perovskite devices did not show significant hysteresis during the voltage scans of the p-i-n solar cells (Figure 5), but the hysteresis grew when the LS-PANI-CSA thickness was increased up to 20 nm because the hysteresis phenomenon in a perovskite-based device depends not only on the characteristics of the perovskite active layer but also on the selective contacts.\(^{86,87}\) The best perovskite device was obtained when the treated HTL was 15 nm thick due to the minimized potential energy loss at the HTL/perovskite interface.

The series resistance \(R_s\) of a device refers to the integral conductivity of all its layers, which is connected to the internal carrier mobility of the device layers.\(^{88}\) Shunt resistance \(R_{sh}\) is the loss of photocurrent through carrier recombination at the interface of each layer of a device.\(^{86,87}\) The untreated LS-PANI-CSA in three p-i-n solar cells showed high \(R_s\) values with the maximum value reaching 109 \(\Omega \text{cm}^2\) at 20 nm of thickness, while the treated LS-PANI-CSA showed lower \(R_s\) values, less than 1 \(\Omega \text{cm}^2\) at 15 nm of thickness, which indicates good interphase contact with high-conductivity device layers, leading
to increased $J_{sc}$ values. The perovskite device based on PEDOT:PSS has a higher $R_s$ with a value of 182 Ω cm$^2$ compared to the treated and untreated LS-PANI-CSA. The untreated LS-PANI-CSA device showed poor $R_{sh}$, which indicates current leakage arising from low perovskite coverage on the HTL. However, in a planar structure, the pinhole within the perovskite allows direct contact between the device layers, leading to a decrease in shunt resistance and finally a drop in the fill factor of the device. We believe that the high roughness and low electrical properties of untreated LS-PANI-CSA were the main reasons for the reduced surface coverage by the perovskite and weaker device performance.

Figure 5e shows the external quantum efficiency (EQE) measurement for the devices between 300 and 800 nm, which was applied to confirm the higher $J_{sc}$ that was harvested from the device with the treated LS-PANI-CSA. Even though transparency of the treated film decreased slightly at a wavelength interval of 550−750 nm compared to the spectra of the untreated film, it is clear that the EQE increased in the visible spectrum overall. It is most clearly explained by the peak at approximately 650 nm in EQE for the untreated films. This peak is not present in the treated films because of the π−polaron absorption band in PANI as a result of some undoping of the polymer backbone. Obviously, the EQE values in the entire range are significantly enhanced by the HTL treatment (Figure 5e). Moreover, it is possible to use the EQE data to perform a check on the validity of the measured solar cell performance and specifically the $J_{sc}$ values. The calculated $J_{sc}$ values from EQE integration over the AM 1.5 solar spectrum are consistent with the measured $J_{sc}$ value, less than 11% difference (Table 1 for treated and Table S1 for untreated HTL devices). This low mismatch has been noted as a good measure of confidence in the measured $J_{sc}$ and hence efficiency values.

In order to gain a broader understanding of the results from the perovskite devices, 15 p-i-n solar cells were analyzed to provide statistical data for three thicknesses of both untreated and treated HTLs. The performances of all the p-i-n solar cells were plotted in Figure S16, ignoring a device that has fabrication defects. As can be seen, devices with untreated 20 nm-thick HTLs displayed an average $J_{sc}$ of 12 mA cm$^{-2}$, $V_{oc}$ of 0.39 V, and FF of 44.8%, resulting in a relatively low PCE of 1.94%, while the untreated 15 nm-thick devices had an average $J_{sc}$, $V_{oc}$, and FF of 14.8 mA cm$^{-2}$, 0.52 V, and 52%, respectively, with a PCE of 3.59%. Reducing the thickness of the untreated LS-PANI-CSA down to 10 nm increased the average FF to 57.3% and lowered the $V_{oc}$ and PCE to 0.41 V and 3.22%, respectively. The photovoltaic performance of the devices was largely improved after the LS-PANI-CSA film was treated with the DMSO solvent treatment. It is clear in Figure S15 that the devices showed high performance with average PCEs of 6.32, 9.64, and 5.41% for 10, 15, and 20 nm thicknesses, respectively.

To avoid interface loss between the cathode and ETL, a thin interlayer of bathocuproine (BCP) was inserted between the PCBM and the metal electrode (Ag) in our inverted device using a solution process. The film thickness of the BCP, calculated using Horiba Jobin Yvon UVISEL ellipsometry, was 5.035 ± 1.533 nm (Figure S14), which is an ideal thickness for use in inverted perovskite devices to prevent charge accumulation at the PCBM/BCP/Ag interfaces. It was impossible to use AFM or SEM to measure BCP thickness because of the highly transparent layer.

For perovskite solar cells, a high-efficiency device may have poor long-term stability due to gradual deterioration under operational conditions or the interface/active layer contact effects. Therefore, stability testing is required to evaluate perovskite device performance. The PCEs of our p-i-n devices with treated LS-PANI-CSA as the HTL showed very good long-term stability when stored in a glovebox for 240 days and exposed periodically to ambient environmental conditions during the test process compared to both untreated and PEDOT:PSS based on perovskite p-i-n devices. As can be seen in Figure 5f, the normalized PCE under simulated sunlight illumination with AM 1.5 G (100 mW cm$^{-2}$) light for untreated LS-PANI-CSA decreased dramatically after half of the stored time compared to the treated LS-PANI-CSA device, while the PEDOT:PSS device showed a shorter lifetime than that of the other devices. XRD (Figure 2g) showed no PbI$_2$ residue when perovskite was deposited onto all HTLs. Therefore, the low stability of the PEDOT:PSS and untreated LS-PANI-CSA perovskite-based device can be attributed to (1) the low hydrophobicity of the HTL (surface properties of HTLs) and (2) undesirable perovskite properties when deposited onto untreated and PEDOT:PSS HTLs. Disregarding the effect of the ferroelectric nature of perovskite materials, treatment of LS-PANI-CSA by DMSO was necessary to increase the hydrophobicity of the HTL and increase the device stability.

**CONCLUSIONS**

We have reported a low-cost, facile, low-temperature, processible LS-PANI-CSA as a new hole-transport layer for inverted planar MAPbI$_3$ solar cells. The HTL’s morphology was improved and work function tuned using DMSO solvent treatment. It was found that the solvent treatment process on the pristine LS-PANI-CSA film can increase polymer hydrophobicity, which is very important for micrometer perovskite grain growth with minimal grain boundaries and the lowest pinhole, compared to the perovskite deposited onto the untreated layer. The thickness of the LS-PANI-CSA was investigated, and the results showed that the ideal LS-PANI-CSA film thickness in this study was ~15 nm; an increase or decrease in thickness resulted in poorer photovoltaic device performance. Moreover, the DMSO-treated LS-PANI-CSA leads to improvement of the stability of the perovskite device due to the treatment process by modifying the surface properties of the LS-PANI-CSA layer with high hydrophobicity. The treatment of LS-PANI-CSA as an HTL can be further developed for large-area or flexible-substrate, high-quality perovskite films in solar cells and other electronic device applications. While the current PCE may be low compared to commercially available HTLs, such as PTAA, and Spiro-OMeTAD, the cost to produce polyaniline-based materials is generally much lower. This is a reason to continue the development of new HTLs, such as LS-PANI to further improve the characteristics for use in PV devices.

**EXPERIMENTAL DETAILS**

**Materials and Methods.** Unless stated otherwise, all materials in this study were purchased from Sigma-Aldrich and used as received.

**Synthesis of LS-PANI.** The synthesis of LS-PANI using oxidative polymerization has been described elsewhere. In brief, 0.5 g of sodium lignosulfonate (Reax 825E, compli-
mentary sample from Ingevity) was dissolved in 50 mL of deionized water, then the solution was constantly stirred for 15 min in an ice bath. To reduce the pH of the protonated sodium solution to 4, concentrated sulfuric acid was added dropwise to the solution. Two milliliters of freshly distilled aniline (weight ratio of aniline to sodium lignosulfonate: 4:1) were then added to the reaction mixture. Adding the monomer to the reaction mixture increased the initial pH. To bring the pH back to 4, H2SO4 was dropped in the reaction mixture again. Next, 2.62 g of sodium persulfate (Na2S2O8) as a precipitate (light blue) was vacuum-constantly stirred in the 0 °C ice bath overnight. The solution was filtered through a 0.2 μm filter paper and washed with distilled water until the filtrate became colorless and had a pH close to 7. The final solid product of lignosulfonate-doped polyaniline was dried under a vacuum at room temperature and stored in a closed vial until use. The pure PANI was synthesized in a similar way but without lignosulfonates to compare to lignosulfonate-doped PANI.

Protonation and Dispersion of LS-PANI. Camphorsulfonic acid (CSA) was used to protonate LS-PANI using solid-state synthesis. Fully protonated LS-PANI was prepared by mixing the powder of 0.062 g of LS-PANI with 0.0750 g of CSA. After grinding, the mixed powder was dissolved in 50 mL of 0.1 M ammonium hydroxide and stirred overnight. Finally, the product was vacuum-filtered through a Whatman #4 filter paper. The wet cake was washed with distilled water until the filtrate was clear then partially dedoped by washing with 15 mL of 1 M ammonium hydroxide (NH4OH). To complete the dedoping process, the polymer was suspended in 50 mL of 0.1 M ammonium hydroxide and stirred overnight. The resulting precipitate (light blue) was vacuum-filtered through a Whatman #4 filter paper. The wet cake was washed with distilled water until the filtrate was clear then partially dedoped by washing with 15 mL of 1 M ammonium hydroxide (NH4OH). 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Surface Topography and Device Layer Thickness Measurements. Surface morphology and film thickness were measured using AFM (Bruker Dimension 3100 Icon FastScan). The tapping mode was applied with a 1 Hz scan rate and different scan sizes (10 μm × 10 μm or 5 μm × 5 μm). The data from the scanned surface was collected using a silicon tip connected to a cantilever (resonance freq.: 300 KHz; force constant: 40 N m⁻¹) moving in three directions. To measure its morphology, LS-PANI-CSA was deposited onto a cleaned glass substrate, and each film was scanned in different locations with a 10 μm × 10 μm scan size. For thickness measurements, the LS-PANI-CSA films were wiped with a wet acetone cotton swab (compressed cotton cleanroom swabs) to get a highly sharp edge over the film surface with a 5 μm × 5 μm scan size at the glass–film interface, and then Nano Scope analysis (version 1.5, Bruker) was utilized for image analyses. All AFM measurements were taken at room temperature with the microscope covered by an acoustic hood to protect it from any vibrational noise. To study the surface topography of perovskite films and a cross section of the device layer, SEM (JEOL JSM 7000F) was used on the area where the perovskite films were deposited onto the treated and untreated LS-PANI-CSA/glass substrate.

To measure the BCP film thickness, Horiba Jobin Yvon UVISEL ellipsometry was used. Note that it is impossible to use AFM or SEM to measure BCP thickness because of the transparent layer. The thickness of the device layers was measured using the SEM cross section.

Tip Calibration and Kelvin Probe Force Microscopy Measurements. To measure work function of the samples, the treated and untreated LS-PANI-CSA films were deposited on the ITO substrate and then grounded onto the AFM stage using silver paste, which helps reduce the error signal and charge build-up phenomena. All the samples were measured in one system run over one set, and the CPD measurements were taken at four random surface spots on each sample to rule out the effects of surface contamination or defects. The dual-pass amplitude-modulated of the Kelvin probe force microscopy (AM-KPFM) or so-called lift mode was performed for surface potential measurement. Using this technique, the surface topography was obtained by the standard tapping mode in the first pass. The line profile is lifted to a set height above the surface for minimizing interference between the tip and the sample (in our case, the lift scan height was 100 nm). In the second pass, the tapping drive piezo was turned off while an oscillating voltage \( V_{AC} \sin(\omega t) \) was applied to the probe. If there is a \( V_{DC} \) voltage difference between the probe tip and sample, then the cantilever will oscillate at the frequency \( \omega \) due to the attractive and repulsive electrostatic interaction \( F_{es} \) between the probe and sample. Therefore, the total electrostatic force (attractive and repulsive) \( F_{es} \) in a capacitor between tip and sample can be expressed by the following equation:

\[
F_{es} = -\frac{1}{2} \frac{\Delta V^2}{dC} \frac{dC}{dZ} = -\frac{1}{2} \frac{dC}{dZ} [(V_{DC} - CPD) + V_{AC}\sin(\omega t)]^2
\]

(3)

where \( V_{DC} \) is the dc bias voltage and CPD is the contact potential difference between the probe and sample.

When the \( V_{DC} \) voltage is applied between the tip and sample, the output signal of the lock-in amplifier is nullified, and \( F_{es} \)
becomes equal to zero. To obtain the value of \( V_{DC} \) for each point on the sample surface, a map of the work function of the whole sample surface area can be composed by monitoring \( V_{DC} \) = CPD, which is then recorded as a surface potential image (contact potential difference between the tip and sample). Here, the measurements were performed in ambient conditions at room temperature and 30–40% relative humidity. Bruker’s SCM-PIT-V2 electrically conductive probe with a platinum-iridium-coated tip with a nominal spring constant was used in the range of \( 3–6 \) N m\(^{-1} \) with a resonant frequency of 75 KH after calibrating with freshly cleaved, highly oriented pyrolytic graphite (HOPG). Treated and untreated LS-PANI-CSA were deposited onto glass/ITO substrates after the substrates had been cleaned and treated with ozone-ultraviolet treatment for 10 min. To measure the work function by KPFM, the glass/ITO/LS-PANI-CSA films were grounded onto the AFM stage using silver paste. To avoid any mistake in CPD results due to surface contamination or tip wear, the CPD measurement procedure was repeated many times using different tips on four surface area spots. The Z range (shaker piezo) was set to 13.7 \( \mu \)m for all measurements with a 5 \( \mu \)m scan size.

**X-ray Photoelectron Spectroscopy (XPS).** The elemental composition of the HTLs (treated and untreated LS-PANI-CSA) and perovskite as a thin film on an ITO-coated glass substrate/HTLs was studied using X-ray photoelectron spectroscopy (Kr\textsubscript{a}, Thermo Scientific, Waltham, MA) with a monochromatic Al K\textsubscript{a} (\( h\nu = 1436.6 \) eV) X-ray source. The X-ray beam was 36 W and 400 \( \mu \)m in diameter. Survey scans (0–1350 eV) were done on each sample at a pass energy (CAE) of 200 eV and a 1 eV step size, and the relative abundance of elements of interest was found using Avantage software.

**Raman Spectroscopy.** Raman measurements were taken for 15 nm-thick HTL films (treated and untreated LS-PANI-CSA) deposited onto the silicon substrate (for calibration with the 521 cm\(^{-1} \) silicon peak) using a Horiba Jobin Yvon LabRam 800 Micro-Raman (Edison, NJ). The spectra were collected using a 632.8 nm laser and a 100X objective lens. The rate of exposure was 2 s, acquisition time was 20 s, and two scans were done for each spot. The spot size was 4 \( \mu \)m \( \times \) 4 \( \mu \)m, and the square rastering duo scan mode was utilized. Two different spots were analyzed on the sample for repeatability, and the data was collected without a baseline process.

**Surface Energy.** The contact angle of the HTLs was measured using an EasyDrop (DSA1) system (Kruess Co.) with the sessile drop method. To measure the sample contact angle, 5 \( \mu \)L of deionized water or DMF/DMSO mixed solvent were dispensed gently via a computer-controlled syringe on four different surface locations of the HTLs/ITO/glass substrates, and then a CCD camera was used to capture images of the droplets on the surface. All the contact angles were measured at room temperature.

**Optical Properties of the HTLs and Perovskite Active Layer.** To study the optical properties of the LS-PANI-CSA and perovskite active layer, transmittance and absorption spectra were recorded using UV–vis–NIR spectroscopy (Shimatzu 3600) at wavelengths ranging from 300 to 1000 nm.

**Device Fabrication and Characterization. Inverted Perovskite Device Fabrication.** Pre-patterned 20 \( \times \) 15 mm ITO pixelated cathode (6 Pixel) glass substrates with a sheet resistance of 20 \( \Omega \) s \(^{-1} \) and 1.1 mm thickness were purchased from Ossila Ltd. The ITO glass substrates were cleaned by sequential sonication in 1% warm Hellmanex in water, deionized water, and isopropyl alcohol (IPA) before being rinsed in deionized water and dried with compressed nitrogen. The last traces of organic residues were removed by ozone-ultraviolet treatment for 10 min. LS-PANI-CSA solution was spin-coated onto the clean ITO glass substrates at different speeds to obtain 10, 15, and 20 nm-thick films. The untreated films were deposited onto the ITO substrate at 6500, 7100, and 7600 rpm (revolutions per minute) for 30 s to create films with a thickness of 20, 15, and 10 nm, respectively, while the treated films were spin-coated at 3400, 4200, and 5300 rpm for 40 s to achieve those corresponding thicknesses. After annealing at 65 °C for 30 min on a hotplate, the treated films received a drop of 0.120 mL of DMSO as static deposition then were directly spun without a standing time at 3000 rpm for 1 min then annealed again on a hotplate at 65 °C for 30 min. Finally, all the films were annealed again by vacuum oven at 78 °C for 12 h. PEDOT:PSS (Al 4083 Ossila) was deposited onto ITO at 6000 rpm for 40 s and then annealed on hotplate at 120 °C for 15 min in ambient air.

Before deposition of the perovskite active layer, the HTL films were wiped from the cathode strip using a wet-acetone cotton swab and covered with captain tape. To deposit the MAPb\textsubscript{I3} perovskite, 50 \( \mu \)L of the solution was spin-coated onto the preheated LS-PANI substrates by a one-step method at 5000 rpm for 25 s. After 8 s of spinning time, 100 \( \mu \)L of the chlorobenzene antisolvent was poured onto the substrate in one shot to wash out the surplus DMF solvent, which helps promote fast crystallization of the perovskite layer. The substrates were then moved to a hotplate under the same environmental conditions as the spin-coater and annealed for 10 min at 100 °C. The spin-coating process was performed in a static way, which means that the solution is dropped onto the substrate before rotation begins. The perovskite deposition was performed at 25–27% relative humidity (RH) controlled through a clean nitrogen-filled glovebox to dry the air within 24–25 °C. Afterward, the LS-PANI-CSA/perovskite substrates were transferred to another nitrogen-filled glovebox (0 ppm of oxygen and moisture) to sequentially deposit both electron transport PC60BM (20 mg mL\(^{-1} \) in chlorobenzene, Acros) and interface layers of bathocuproine (BCP, 0.5 mg mL\(^{-1} \) in anhydrous ethanol, Acros) by spin-coating at 2000 rpm for 30 s and 6000 rpm for 10 s, respectively. Finally, 100 nm-thick silver counter electrodes were evaporated using an Angstrom thermal evaporator at 10\(^{-6} \) Torr and deposited at a low deposition rate (0.1 Å s\(^{-1} \)) to avoid penetrating the device layers. After electrode deposition, one drop of UV-curable epoxy (E131, Ossila Ltd.) was deposited onto the center of the device. A glass slide (C181, Ossila Ltd.) was then placed onto the epoxy droplet, and the epoxy was cured under a UV light source.

**Device Characterization.** Devices were tested under ambient conditions (65% RH ± 5%), and the current–voltage (\( J-V \)) measurements were performed under a 1.5 AM sunlight simulator with incident light power of 100 mW cm\(^{-2} \) (PV Measurements, Inc.). An NREL-certified silicon reference cell was used to calibrate the integrated light output from the simulator to 100 mW cm\(^{-2} \) at 25 °C, and a Keithley 2400 source meter was used for electrical measurements. An aperture mask (0.0256 cm\(^{2} \)) was placed over each solar cell to accurately define the device area and minimize absorption of stray light. LabView software was used to sweep voltages from \(-1 \) to +1 V for the forward scan and from +1 to \(-1 \) V for the reverse scan at a rate of 0.4 V/s then Igor software was used to...
analyze the $J-V$ curve. External quantum efficiency measurements were performed using a spectral-responsive system (Bentham model PVE 300).

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