A variety of solar energy conversion systems have emerged as attractive candidates to establish fossil-fuel-free energy networks. Among these, organic solar cells offer the promise of lightweight, flexible, large-area, and cost-effective photovoltaic technology. But, they are not as efficient and stable as their inorganic counterparts. To solve this problem, the concept of a neutral polymeric hole transporting layer (HTL) deposited via oxidative chemical vapor deposition (oCVD) is realized for the first time, by integrating patterned Cl-doped poly(3,4-dimethoxythiophene) thin films into organic photovoltaic devices (OPVs) via a vacuum-based polymer vapor printing technique—oCVD combined with situ shadow masking. Due to this novel polymer’s neutrality, high transparency, good conductivity, and appropriate energy levels, the efficiency and stability of OPVs are remarkably boosted compared to those of OPVs depending on the commercial hole transporting polymer, poly(3,4-ethylene dioxythiophene):polystyrene sulfonate (PEDOT:PSS).

In conventional OPVs, thin photoactive organic layers are sandwiched between the anode and cathode. The interlayer between photoactive organics and anode has a significant impact on the performance of OPVs. The transparency influences the light absorption of photoactive organics while the energy levels and charge transport characteristics impact photogenerated hole extraction and collection. Consequently, the anode interlayer’s properties have a direct effect on the performance parameters of OPVs, such as open-circuit voltage ($V_{OC}$), short-circuit current density ($J_{SC}$), fill factor (FF), and the final power conversion efficiency (PCE).

In order to optimize the performance parameters, HTLs of various composition have been applied to the anode interlayer. Among them, PEDOT:PSS has been the most popular because of its deep work function (i.e., suitable highest occupied molecular orbital [HOMO] level for various organic donor materials), high transparency in the visible-light region, solubility for spin-coating, mechanical flexibility, and earth-abundant element composition (i.e., C, H, O, and S). However, due to the PSS dopants, PEDOT:PSS has a strong acidic nature. This high acidity corrodes photoactive organics and anode materials, and finally damages the PCE and lifetime of OPVs. In this regard, a new neutral hole transporting polymer should be developed to improve the stability of OPVs.

Poly(3,4-dimethoxithiophene) (PDMT) can be an appropriate neutral alternative to PEDOT:PSS because PDMT also has deep work function, high transparency, mechanical flexibility, and the same earth-abundant element composition (i.e., C, H, O, and S). However, PDMT has two major shortcomings limiting its incorporation into OPVs as a HTL. First, its conductivity is too low to promote photogenerated hole transport from HOMO levels of photoactive organics to anode. Second, PDMT’s poor solubility prohibits solution processing, thereby rendering its thin-film fabrication on targeted substrates more complex and difficult. Although there are several previous studies to make PDMT thin-films using electrochemical polymerization, it is not easy for electrochemical polymerization to control the conductivity, uniformity, thickness, and pattern shape of polymer thin-film products.

To resolve the abovementioned issues, we used oCVD technique integrated with situ shadow masking. Unlike other standard methods (e.g., spin-coating, electrochemical polymerization, etc.), oCVD offers a groundbreaking substrate-independent fabrication route to insoluble or infusible polymers because it is a solvent-free, vacuum-based technique enabling conformal thin-film coating of varied conjugated polymers in a single dry step. Specifically, oCVD is a single-dry-step process to simultaneously synthesize, deposit, and dope conjugated polymers on a wide array of substrates at low temperature ($\leq 100 ^\circ$C) in controllable patterns, aligned with situ shadow masking. Moreover, oCVD still maintains vacuum processing benefits, such as well-defined thickness control and uniformity, conformal coverage, parallel and sequential deposition, and inline convertibility with other standard vacuum processes (e.g., thermal evaporation). Recently, this versatile technique has materially advanced its applicability to fabricate diverse semiconducting/conducting polymer thin films for organic electronics.
Based on the abovementioned strengths of oCVD, we successfully made patterned PDMT thin films on nonconductive substrates for the first time. As Figure 1a shows, 3,4-dimethoxythiophene monomer vapor is oxidatively polymerized in the presence of iron (III) chloride oxidant, and at the same time PDMT is deposited on a diversity of substrates, placed on the temperature-controlled stage of the oCVD reactor. The PDMT thin-film thickness is easily controlled by adjusting the polymer-deposition time. The FTIR spectrum of the oCVD-processed PDMT film in Figure 1b clearly identifies the representative functional groups of PDMT (alkyl C–H stretch [3000–2850 cm⁻¹], aromatic C=C stretch [1500–1400 cm⁻¹], C=O stretch [1320–1000 cm⁻¹], aromatic C–H bending [860–750 cm⁻¹], and C–H out-of-plane vibrations [≈690 cm⁻¹]). Also, the Raman spectrum in the Supporting Information (Figure S1) displays the key functional groups of PDMT. These outcomes are well-matched with PDMT’s previously reported characterization data, and thus confirm that PDMT films are successfully synthesized via oCVD.

As the synthetic route in Figure 1c depicts, the oxidative polymerization accomplished by oCVD generates a conducting doped-form PDMT through over oxidation forming polarons and bipolarons. The doped-form PDMT has cations (S⁺), charge-balanced by counter anions (Cl⁻). Thanks to the Cl⁻ anion dopants from iron (III) chloride oxidant, the doped PDMT has good conductivity (≈10 S cm⁻¹) without acidity, unlike PEDOT:PSS. Moreover, doped-PDMT thin films have as high transparency as PEDOT:PSS thin films, as illustrated in Figure 2a,b. Additionally, the transmittance data in Figure 2a,b reveal that the onset of optical absorption by doped PDMT appears at 460 nm, which corresponds to the optical bandgap of 2.7 eV. This means if doped-PDMT thin films possess a proper HOMO level, they can be deployed to OPVs as HTLs, because they are transparent enough to allow photoactive organics to have sufficient light absorption.

To determine the HOMO level of PDMT, cyclic voltammetry (CV) was conducted using the standard three-electrode setup. The resulting CV curve for PDMT is shown in Figure 2c. Based on the curve, the HOMO level is located by following previously published procedures. The onset of the oxidation peak is –0.3 V versus Fc/Fc⁺. The HOMO is then calculated by the following Equation (1), assuming the redox potential of Fc/Fc⁺ is –5.1 eV, relative to vacuum:

$$E_{\text{HOMO}} = -(E_{\text{onset}} \text{ oxidation vs Fc/Fc}^+) + 4.8 \text{(eV)} \quad (1)$$

The calculated HOMO level is –5.1 eV, and the lowest unoccupied molecular orbital (LUMO) level of PDMT is estimated to be –2.4 eV by adding the optical bandgap of 2.7 eV to the HOMO level. Taking the estimated HOMO and LUMO levels into account, the schematic energy-level alignment of DBP (dibenzo-tetraphenyl-perifl anthene)/C₆₀ solar cells with PDMT HTLs is drawn in Figure 2d. The schematic alignment verifies that doped PDMT has an appropriate HOMO level for forming an Ohmic contact between photoactive organics (DBP and C₆₀) and anode (ITO, indium tin oxide), thereby promoting photogenerated hole transport from the HOMO levels of DBP and C₆₀ to the ITO anode. Further, the HOMO and LUMO levels of

Figure 1. a) Schematic of oCVD reactor, b) FTIR spectrum of oCVD-processed PDMT film, and c) synthetic route from 3,4-dimethoxythiophene to over-oxidized PDMT, with undoped and doped PDMT film photos.
doped PDMT match well with the band structure of a variety of photovoltaic materials, including perovskites (methylammonium lead halides), diverse types of quantum dots, and a variety of inorganic semiconductors.

In addition, thanks to the conformal and dry nature of oCVD polymer coating, PDMT film over 20 nm in thickness have smooth surfaces, as the AFM images in the Supporting Information (Figure S2) illustrate. This smoothness is vital for optimizing series and shunting resistances ($R_S$ and $R_{Sh}$) within OPVs as well as preventing unwanted short circuits between the front and back surface contacts of OPVs.

All of the above physicochemical characterization results confirm the candidacy of oCVD PDMT thin films as a neutral HTL for replacing acidic PEDOT:PSS. Therefore, neutral PDMT was next integrated into OPVs for the first time using the polymer vapor-printing technique (i.e., oCVD combined with in situ shadow masking). As the device diagram in Figure 3a exhibits, we employed the conventional single-bilayer-heterojunction architecture, consisting of glass substrate having a 75 nm thick ITO anode, a 25 nm thick electron-donating DBP layer, a 40 nm thick electron-accepting $C_{60}$ layer, a 7.5 nm thick hole-blocking BCP layer, and a top-capping Ag cathode, 100 nm in thickness.

We tested a range of thicknesses of PEDOT:PSS and PDMT HTLs to understand, compare, and optimize how the two HTLs affect the DBP/$C_{60}$ solar cell function. Figure S3 in the Supporting Information displays how the DBP/$C_{60}$ solar cell PCE varies with PEDOT:PSS and PDMT HTL thickness with all other layer thicknesses fixed. While PDMT HTL thickness change has a remarkable influence on the PCE, PEDOT:PSS HTL thickness change does not. The optimum thickness to maximize the PCE is 36 nm for PDMT HTLs, and 31 nm for PEDOT:PSS HTLs. Under these best thickness conditions, the maximum PCE is 4.1% for employing PDMT HTLs, and 3.5% for using PEDOT:PSS HTLs, as the current density versus voltage ($J-V$) characteristics in Figure 3b describe. To the best of our knowledge, 4.1% is the highest PCE record achieved by conventional DBP/$C_{60}$ bilayer-heterojunction solar cells.[10,24,25]

When comparing the performance parameters, as shown in Figure 3c,d, it becomes clear that 36 nm thick PDMT HTLs perform better than 31 nm thick PEDOT:PSS HTLs by enhancing the FF and $J_{SC}$ of the DBP/$C_{60}$ solar cells. Meanwhile, there is no significant difference in the $V_{OC}$ between PEDOT:PSS and PDMT HTLs, after reaching its peak value (0.85–0.88 V). The physical mechanisms that PDMT HTLs enable the higher $J_{SC}$ and FF than PEDOT:PSS HTLs will be discussed next.

To have more systematic understanding on the improvement in $J_{SC}$, dark $J-V$ characteristics (Figure 4a) and EQE (external quantum efficiency) spectra (Figure 4b) were measured. Dark $J-V$ characteristics of the champion devices are plotted on a semilog scale. A 36 nm thick PDMT HTL generates much lower dark $J$ under forward bias than 31 nm thick PEDOT:PSS HTL by a factor of ~100. This consequence indicates the PDMT HTL achieves better interface (Ohmic) contact with less dipoles/carrier traps between DBP and ITO, thereby contributing to the reduction of carrier recombination and the suppression of leakage currents.[26] This mechanism...
Figure 3. a) Device diagram of DBP/C₆₀ solar cells with PDMT HTLs. b) $J$–$V$ characteristics of champion devices under AM 1.5G irradiation, c) PCE and FF, d) $J_{SC}$ and $V_{OC}$ for varying PEDOT:PSS/PDMT HTL thickness (symbols: average values of 6–10 devices, error bar: maximum and minimum values).

Figure 4. a) Dark $J$–$V$ characteristics of champion devices, b) EQE spectra of champion devices with absorption coefficients of DBP and C₆₀, c) $R_s$ and $R_{th}$ for varying PEDOT:PSS/PDMT HTL thickness (symbols: average values of 6–10 devices, error bar: maximum and minimum values), and d) evolution of normalized performance parameters with respect to storage time under N₂ atmosphere.
is further supported by the EQE spectra, where the device quantum efficiency for PDMT is higher over the wavelength range from 375 to 500 nm as compared to PEDOT:PSS. This result reveals that the hole-electron pairs produced by 375 to 500 nm wavelength photons are more effectively separated, extracted, and collected with the PDMT HTL rather than the PEDOT:PSS HTL, mainly due to PDMT’s neutrality. In addition, the EQE spectra shape is well matched with a combination of the absorption coefficient curves of DBP and C$_{60}$, which confirms that the photocurrent originates from photon to electron conversion by DBP and C$_{60}$.

The mechanism enabling PDMT HTLs to improve the FF is closely related to the variation of series and shunting resistances ($R_S$ and $R_{Sh}$) within the DBP/C$_{60}$ solar cells. Specifically, as $R_S$ becomes smaller, FF increases. In contrast, the more $R_{Sh}$ increases, the bigger FF grows. As the visualized data in Figure 4c illustrate, 36 nm thick PDMT HTLs ($≈12$ Ω cm$^{-2}$) realize lower $R_S$ than 31 nm thick PEDOT:PSS HTLs ($≈35$ Ω cm$^{-2}$), and both of them hit the minimum $R_S$ at their ideal thickness. However, there is a different trend for $R_{Sh}$. As PDMT HTLs approach their optimum thickness, $R_{Sh}$ spikes to its summit ($≈6440$ Ω cm$^{-2}$), whereas $R_{Sh}$ with PEDOT:PSS HTLs remains almost steady (1200–1280 Ω cm$^{-2}$) irrespective of their thickness. Consequently, the contact resistance dynamics with PDMT HTLs is much more advantageous than that with PEDOT:PSS HTLs for raising the FF.

PDMT’s beneficial contact resistance dynamics results from oCVD’s unique merits, enabling direct anion dopant injection into conjugated polymer chains as well as conformal polymer thin-film coating on patterned target substrates in a single dry step. The PSS dopants in PEDOT:PSS generate protons (H$^+$), as drawn in Figure S4 of the Supporting Information. As the proton concentration increases, although the conductivity of PDMT:PSS HTLs can increase, the photogeneration hole mobility in PEDOT:PSS HTLs can decrease due to the scattering between protons and holes. The reduced hole mobility elevates the interfacial energy barrier for photogenerated hole transport from DBP to ITO, and finally $R_S$ grows. On the other hand, the proton-free Cl$^-$ dopants in oCVD-processed PDMT just augment the conductivity in PDMT HTLs without any scattering effect, and thus minimize the interfacial energy barrier and $R_S$.

The maximized $R_{Sh}$ by 36 nm thick PDMT HTLs is most likely explained by the conformal and dry nature of oCVD polymer coating. In the case of spin-coating method, dewetting defects (e.g., pinholes, fissures, cracks, etc.) are inevitable, and they cause unwanted short circuits between the front and back surface contacts of OPVs. However, oCVD polymer coating technique rarely results in the dewetting defects because oCVD is a solvent-free vapor-phase polymer treatment. Hence, 36 nm thick PDMT HTL attains much higher $R_S$ than 31 nm PEDOT:PSS HTL by a factor of $≈5$. PDMT HTL thicknesses over or under 36 nm have smaller $R_{Sh}$ owing to rougher surfaces (Figure S2, Supporting Information). In particular, for under 36 nm thick PDMT HTLs, tunneling effects are more significant and reduce $R_{Sh}$.

Compared to acidic PEDOT:PSS, another overwhelming benefit is PDMT’s neutrality, which improves the device lifetime (Figure 4d). Beyond the demand of high efficiency, long-term device stability is another linchpin requirement to commercialize OPVs. To evaluate the champion devices’ stability as a function of time, continual and periodic PCE measurements were carried out under N$_2$ atmosphere. The device with the neutral PDMT HTL maintained 83% of its optimum efficiency after 17 d, while the device with the acidic PEDOT:PSS HTL retained only 12% of its best efficiency. When checking how the performance parameters changes as time goes by, it is obvious that $V_{oc}$, $J_{sc}$, and FF with the acidic PEDOT:PSS HTL drops much faster than those with the neutral PDMT HTL, although there are fluctuations.

This is because of the intense acidity of PSS dopants, which produce protons. The protons destroy surrounding photoactive organics and anode materials (e.g., DBP and ITO), and finally damages the device performance. Meanwhile, the proton-free Cl$^-$ dopants in oCVD-processed PDMT guarantee the neutral nature, where all kinds of molecular components in OPVs can play their own roles properly and sustainably as long as possible.

In conclusion, oCVD unlocks the potential of PDMT in organic electronics by securing a solvent-free facile path to fabricate conformally patterned PDMT thin films on diverse substrates for the first time. Here we have demonstrated PDMT thin films incorporated into DBP/C$_{60}$ solar cells, as neutral HTLs create a suitable alternative to acidic PEDOT:PSS HTLs. The oCVD-processed PDMT HTL exhibits the highest reported $J_{sc}$, FF, and PCE of single-bilayer DBP/C$_{60}$ solar cells as a result of its good conductivity, high transparency, appropriate energy levels, and neutrality. Notably, oCVD PDMT coating’s conformal and dry nature with anion dopant injection capability creates a hole transport-favorable interface, minimizing dipoles/carrier traps, scattering effects, interfacial energy barrier, dewetting defects, carrier recombination, and thus leakage currents. Consequently, the high-quality Ohmic contact with minimized $R_S$ and maximized $R_{Sh}$ is formed between DBP and ITO, to upgrade the $J_{sc}$, FF, and PCE. Furthermore, the neutral nature of oCVD-processed PDMT remarkably extends the solar cell lifetime. These outcomes represent the first example to substantiate the concept of a neutral hole transporting polymer, which is promising for achieving enhanced solar cell efficiency and lifetime. Finally, the findings from this study are also applicable for other categories of electronic devices with different architectures (e.g., inorganic solar cells, quantum dot solar cells, perovskite solar cells, organic light emitting diodes, and photoelectrochemical cells), because oCVD is a versatile polymer-coating technique, independent of material solubility and substrate properties.

**Supporting Information**

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

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