Molecular Interface Engineering via Triazatruxene-Based Moieties/ NiO_x as Hole-Selective Bilayers in Perovskite Solar Cells for Reliability

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Interface engineering is an effective approach to decrease nonradiative recombination and the energy barrier at the perovskite/hole transporting layer (HTL) interfaces. To overcome such limitations, an organic semiconductor (DTT-EHDI₂) is proposed, which is, composed of dithienothiophene (DTT) as the core and a planar triazatruxene incorporating an alkyl chain as the side group. This is noted to be an effective interfacial layer for inverted planar perovskite solar cells (PSCs). The altered interface effectively minimizes the detrimental charge recombination and tailors the photoinduced charge transfer dynamics at the interface of the inorganic HTL/perovskite. The π -conjugation in DTT-EHDI₂ induces high hole mobility and electrical conductivity via electron-donating properties and strong π - π intermolecular interaction. The synergetic approach leads to a substantial performance enhancement in dopant-free DTT-EHDI₂-based inverted planar PSCs, achieving 18.15% power conversion efficiency with negligible hysteresis effect. The present approach provides an effective direction of the cost-effective thiophene derivative as an interfacial agent to escalate the optoelectronic performances in photovoltaics.

1. Introduction

Perovskite solar cells (PSCs) is an emerging photovoltaic (PV) technology with the potential to disrupt the conventional silicon

solar cell market owing to their excellent progress in performance and easy fabrication steps. The power conversion efficiencies (PCEs) of PSCs reached 25.5% using the regular (n-i-p) structure since their debut in 2009.^[1–3] However, the PCE of inverted (p-i-n) PSCs still lags behind that of n-i-p-structured devices.^[4,5] The notable strategies have been devoted including new device architectures, perovskite compositional and interfacial engineering, and used of rational materials derived from inorganic oxides, organic molecules, and 2D materials to tune PSCs' electro-optical properties and subsequently boost PV performance and stability.^[5–11] Typically, PSCs are composed of a light-harvesting perovskite as an active layer sandwiched between two selective charge-transporting layers, namely the hole-transporting layer (HTL) and the electron-transporting layer (ETL) for positive and negative charge

extraction, respectively. These charge-transporting layers are rationally selected by taking into consideration the charge mobility, energy-level alignment, and compatibility with the perovskite absorber.^[12,13] As PSCs are composed of several layers, interfaces play a pivotal role in their operation, determining the overall performance and stability.^[14] The energy barriers, defects or charge/ion accumulation, and undesired charge transfers at interfaces, interfacial vacancies, and recombination greatly impact electrical performances and hysteresis in the PSCs, and such issues can be addressed by interface engineering to overcome problematic aspects.^[14–17]

In particular, the frequently used HTLs in planar p-i-n PSCs are poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)-{PEDOT:PSS} and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] {PTAA}.^[7,18,19] However, the hygroscopic nature and highly acidic property associated with PEDOT: PSS accelerate the degradation of the perovskite layer and compromise the long-term PSCs stability.^[20,21] Further, perovskite shows appalling film coverage on severe nonwetting HTL such as pristine PTAA, which renders PSCs with poor short-circuit current density (J_{sc}) and fill factor (FF).^[22] In contrast, PSCs using NiO_x nanocrystals (NCs) as HTL exhibited excellent stability under prolonged operational conditions.^[23] Though intrinsic NiO_x is

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DOI: 10.1002/solr.202100793

a wide-bandgap (>3.5 eV) semiconductor with high hole mobility, it suffers from weak built-in field strength and large energy-level offset at the interface of NiO_x /perovskite due to limited hole concentration and the wide gap between Fermi level and its valence band maximum (VBM).^[4,24,25] The large energy-level offset at the interface can result in the hole accumulation at the HTL/perovskite interface, thus with the possibility of photo-induced charge recombination at the interface.^[26] To minimize this, considerable efforts have been laid to improve the energy band alignment which in turn can enhance photoinduced charge transfer dynamics at the NiO_x /perovskite interface through the incorporation of an interfacial layer.

Selecting a core structure through the molecular design of hole transport materials (HTMs) for PSCs is a critical factor, which impacts various properties and affects the PV performances.^[27] Spiro-OMeTAD (2,2',7,7'-tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene) is a spiral-core-based organic molecule, which has been widely utilized as the standard HTM in *n*-*i*-*p* PSCs, owing to the aligned energy level with perovskite, and inhibits aggregation together with excellent thermal stability and film-forming ability.^[28] However, organic molecules based on spiral core show poor regularity of the structural arranging, adopting amorphous nature and thus ensuring lower hole mobility and conductivity.^[27] Typically, spiral core-based HTMs including Spiro-OMeTAD in their pristine state cannot be used and require *p*-type dopant and additives to enhance their hole conductivity for the fabrication of efficient PSCs, yet the hygroscopic nature of these additives is a tradeoff and promotes device instability through moisture-induced degradation of the perovskite layer.^[29] In this context, planar molecules are preferred to be arranged in regular order with proper intermolecular π - π interaction, yielding higher hole mobility, charge transport, and extraction, and eventually boosting the PCE of PSCs.^[27,29,30] However, the ease of crystallization associated with planar-core molecules adversely affects obtaining the uniform film, solubility, and protection of perovskites from moisture.^[27,31] To achieve a balance between PSCs' stability and PV performances, crystallinity and amorphism should be carefully adjusted by selecting suitable core structures and substituents during molecular design. Thiophene-based derivatives as HTM have been extensively utilized since the electron-rich sulfur atoms in thiophene render a strong electron donor character, that facilitates efficient charge transport.^[32–34] In addition, the high polarizability of sulfur atoms and lower stabilization energy in thiophene rings allows the stabilization of the conjugated chain and reduces the energy level, and subsequently enhance the charge transport properties, accelerating the extraction of holes from the surface of the perovskite.^[32,34] Planar nitrogen-containing triazatruxene (TAT) came out as a promising donor core unit or side group for organic molecules owing to the tunable electro-optical properties.^[35–40] TAT is a synthetically versatile constituent with three indole units fused to a benzene ring in a π -conjugated structure that provides a route to high hole mobility as a consequence of electron-donating properties and strong π - π intermolecular interaction.^[37] Moreover, the three indole cores in the TAT building block can be easily modified to increase stability and solubility.^[35] However, hitherto, the behavior of thiophene and TAT-based molecules has not been thoroughly studied as an interfacial layer in inverted PSCs.

Owing to its intriguing properties, we designed and synthesized organic molecules labeled as **DTT-EHDI**₂, with dithieno[3,2-*b*:2',3'-*d*]thiophene (DTT) as the core and 5,10,15-tris(2-ethylhexyl)-10,15-dihydro-5H-diindolo[3,2-*a*:3',2'-*c*]carbazole (EHDI) as substituents. The molecularly engineered **DTT-EHDI**₂ was incorporated in planar *p*-*i*-*n*-type PSCs as an interfacial layer between the NiO_x and perovskite. The π -bridge between the thiophene core and the donor groups renders high performance in PSCs indicating 18.15% PCE and exhibiting a significant 9% performance increment to that of the reference PSCs (16.66%).

2. Results and Discussion

The synthetic protocol for **DTT-EHDI**₂ is represented in **Figure 1a**, and the step-by-step synthetic procedure is documented in the Experimental Section. The fused thiophene core was purchased commercially. **DTT-EHDI**₂ was synthesized by Pd-mediated Suzuki coupling reaction between 2,5-dibromothiophene[3,2-*b*]thiophene and TAT-boronic ester in 98% yield and characterized by NMR (¹H and ¹³C) and matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) spectrometric studies. The NMR spectral patterns and their relative integration values of **DTT-EHDI**₂ are consistent with the molecular structure (Figure S1, and S2 Supporting Information). Moreover, the solubility test of the compound was conducted in several organic solvents including toluene, chlorobenzene (CB), dichloromethane (DCM), dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO). The UV-visible absorption spectrum of **DTT-EHDI**₂ was recorded in DCM solvent and the solid thin film (Figure 1b), which exhibits a maximum at 435 nm, that can be attributed to the intramolecular charge transfer of the π - π^* transition.^[35] In the case of thin films, an expectedly slight redshift in the band edge is noted due to the molecular stacking between the **DTT-EHDI**₂ molecules.^[35]

Further, the thermal stability of **DTT-EHDI**₂ was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements (Figure S3a,b Supporting Information). The TGA curve of **DTT-EHDI**₂ exhibits decomposition temperature (*T*_d) close to the 380–420 °C range, possessing unique thermal stability. *T*_d was calculated at the 5% weight loss for the molecule in the second cycle of heating as a preheat cycle was performed to eliminate possible humidity or impurities trapped in the material. The glass transition (*T*_g) was estimated to be around 200 °C with the melting temperature at around 310 °C. No crystallization was observed during cooling and thus we can speculate that the **DTT-EHDI**₂-based PSCs will ensure the operational viability at extreme conditions (>85 °C).

We investigated the electrochemical properties of **DTT-EHDI**₂ using cyclic voltammetry (CV) experiments, measured in dichloromethane at room temperature ($c \approx 1 \times 10^{-3}$ M) with tetrabutylammonium hexafluorophosphate (TBAPF) (0.1 M) as supporting electrolyte (Figure S4, Supporting Information). To achieve a higher open-circuit voltage, the energy levels of **DTT-EHDI**₂ should be appropriate to the perovskite energy levels. The highest occupied molecular orbital (HOMO) energy level of **DTT-EHDI**₂ was estimated from the first oxidation potential using the equation $E_{(\text{HOMO})} = -4.4_{(\text{vs. vacuum})} - (E_{1/2\text{ox}} \text{ vs. (Fc/Fc}^+)) = -5.340$, where $E_{1/2\text{ox}}$ is the onset oxidation potential

Figure 1. a) Synthetic route for **DTT-EHDI₂** (2,6-bis(5,10,15-tris(2-ethylhexyl)-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazol-3-yl)dithieno[3,2-b:2',3'-d]thiophene), b) UV-vis absorption spectra of **DTT-EHDI₂** in solution (black curve) and in film (red curve) deposited on NiO_x thin film, and c) energy band alignment at the NiO_x/CsFAMA interface.

(0.94 eV) considering the correction of Fc/Fc⁺ versus normal hydrogen electrode (NHE, 0.70 eV). To note here, the CV graph has already been shifted considering the Fc/Fc⁺ in TBAPF correction. The optical bandgap (E_g) of the HTM is estimated from the onset wavelength of the absorption of **DTT-EHDI₂** in solution, which is 490 nm; thus, $E_g = 2.53$ eV. From this we calculated the lowest unoccupied molecular orbital (LUMO), as $\text{HOMO} - E_g = -5.34 \text{ eV} + 2.53 \text{ eV} = -2.81 \text{ eV}$. The calculated HOMO level for **DTT-EHDI₂** (-5.34 eV) is suitable with the valence band of Cs_{0.1}(FA_{0.9}MA_{0.1})_{0.9}Pb(I_{0.9}Br_{0.1})₃, which is assumed as -5.80 eV, as reported by Wu et al. for triple-cation perovskites.^[41] The LUMO level was found to be -2.81 eV, which is beneficial to overcome the undesirable electron transfer from perovskite to the HTL. The energy bandgap between the HOMO and LUMO of **DTT-EHDI₂** was measured to be 2.53 eV. The valence band maximum of NiO_x NC film is -5.21 eV, which is about 0.13 eV higher compared with the HOMO level of **DTT-EHDI₂**, indicating a narrow energy barrier for hole transfer between perovskite/NiO_x^[25] (Figure 1d), and will form a beneficial spike structure.

The X-ray diffraction (XRD) pattern of as-synthesized NC NiO_x exhibits a cubic crystal structure with the characteristic diffraction peaks at 37.18°, 43.28°, and 62.42° corresponding to the (111), (200), and (220) planes (Figure S5, Supporting Information).^[23,42] The estimated optical bandgap derived from UV-vis of the NiO_x film was 3.45 eV (Figure 2a). Owing to the high absorption and higher thermal stability, triple-cation

perovskite (FA, MA, and Cs) was used as a light harvester to fabricate PSCs.^[25] The microstructures of the NC NiO_x film and **DTT-EHDI₂** deposited on FTO were investigated by scanning electron microscopy (SEM), as illustrated in Figure 2b,c, respectively. Notably, we observed that the grain size of perovskite grown on **DTT-EHDI₂**/NiO_x is slightly larger and uniform than that on NiO_x only (Figure 2d,e). The enhanced grain growth could be attributed to the lower wettability of **DTT-EHDI₂** compared with NiO_x that tends to shrink the number of nucleation sites in the perovskite and provides extra space for larger grain growth during annealing, resulting in diminishing the trap states and possible recombination pathways.^[43,44] The contact angles of the perovskite precursor on NiO_x and **DTT-EHDI₂**/NiO_x were measured to be 33 ± 1° and 58 ± 1° (Figure S6, Supporting Information), suggesting the role of the **DTT-EHDI₂** layer in the surface property. We probed the surface with scanning probe microscopy (SPM) to evaluate the surface microstructure and roughness of NiO_x and **DTT-EHDI₂**/NiO_x. Arguably, the interfacial properties (Figure S7, Supporting Information) impact the charge-transporting properties. We noted that root-mean-square (RMS) roughnesses of the NiO_x and **DTT-EHDI₂**/NiO_x films are 35.77 and 24.59 nm, respectively, crediting surface smoothness upon **DTT-EHDI₂** deposition. The surface topography and phase images (Figure S8, Supporting Information) of the perovskite deposited on different surfaces, where the perovskite displays uniform and significantly reduced RMS roughness (31.77 nm) on **DTT-EHDI₂**/NiO_x, as compared with that of the

Figure 2. a) UV-vis absorption spectra of NiO_x film; inset shows the calculated optical bandgap from the Tauc plot. Top-surface SEM images of b) NiO_x film, c) DTT-EHDI₂ deposited on NiO_x film, and CsFAMA grown on d) NiO_x film and e) DTT-EHDI₂/NiO_x NC film. To note here, images (b) and (c) are in 90 K magnification, while (d) and (e) are in 60 K magnification. f) XRD patterns of CsFAMA perovskite deposited on NiO_x film and DTT-EHDI₂/NiO_x film.

perovskite on NiO_x (40.44 nm). The DTT-EHDI₂ assisted in perovskite crystallization, which is favorable for effective charge extraction. Diffractograms were recorded to decipher the crystal structure of the perovskite (Figure 2f), in which the predominant peak appears at 14.1° in both situations corresponding to the (101) crystal plane of CsFAMA; this indicates the suitable crystallinity of the perovskite. In the UV-vis absorption spectra (Figure S9, Supporting Information), the absorption edge of the films largely remains unchanged upon interface engineering with DTT-EHDI₂.

The influence of the thin film of DTT-EHDI₂ on the charge transport properties of NiO_x as HTLs was probed by measuring their thin-film *I*-*V* profile, in FTO/NiO_x/Au and FTO/NiO_x/DTT-EHDI₂/Au configurations in the dark (Figure 3a). The conductivity of NiO_x/DTT-EHDI₂ was $37.59 \times 10^{-6} \text{ S cm}^{-1}$, similar to NiO_x ($28.24 \times 10^{-6} \text{ S cm}^{-1}$). The hole mobility of NiO_x with and without DTT-EHDI₂ interfacial layer was 2.78×10^{-5} and $6.91 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, derived from semilogarithmic *J*^{0.5}-*V* curves of the hole-only devices in the dark (Figure 3b) via the classical Mott-Gurney

Figure 3. a) *I*-*V* curves for conductivity measurements in the configuration of FTO/NiO_x/Au and FTO/NiO_x/DTT-EHDI₂ in the dark and b) *J*-*V* curves for hole-mobility measurements with the hole-only device with the configurations of FTO/PTAA/NiO_x/Au and FTO/PTAA/NiO_x/DTT-EHDI₂/Au in the dark.

space-charge-limited-current (SCLC) law: $J = 9\epsilon\epsilon_0\mu V_{app}^2/8L^3$. Here, ϵ_0 , ϵ , and L represent the dielectric constant of free space, the relative dielectric constant, and the thickness of the charge transport layer, respectively.^[45] The dielectric constant for NiO_x was taken as 4.8.^[46] We estimated the hole mobility of DTT-EHDI_2 and noted it to be $1.12 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Figure S10, Supporting Information).

We assessed DTT-EHDI_2 as an interfacial layer in planar PSCs with a device architecture, $\text{FTO}/\text{NiO}_x/\text{DTT-EHDI}_2/\text{Cs}_{0.1}(\text{FA}_{0.9}\text{MA}_{0.1})_{0.9}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3/\text{PCBM}/\text{BCP}/\text{Ag}$ (Figure 4a). The cross-sectional SEM image of PSCs with the interfacial layer of DTT-EHDI_2 (Figure 4b) reveals an interconnected and sandwiched structure of NiO_x ($\approx 70 \text{ nm}$) and DTT-EHDI_2 ($\approx 20 \text{ nm}$), together with a $\approx 400 \text{ nm}$ -thick perovskite layer. The typical

current-voltage (J - V) curves of the PSCs with and without the interfacial layer are shown (Figure 4c) and the corresponding PV parameters are represented in Table 1. It can be deduced from the reverse scan J - V curves that the DTT-EHDI_2 interface layer enabled the V_{OC} , J_{SC} , and FF of the PSCs to increase from 1000.13 mV, 22.79 mA cm^{-2} , and 72.96% to 1034.09 mV, 23.18 mA cm^{-2} , and 75.71%, respectively. Subsequently, DTT-EHDI_2 -based PSCs yielded an overall PCE of 18.15% with an average PCE of 17.93%, while the control PSCs showed a maximum PCE of 16.66%. Furthermore, the incident photon-to-current efficiency (IPCE) spectrum and the achieved integrated current densities (J_{int}) of 21.42 and 21.79 mA cm^{-2} for devices with and without DTT-EHDI_2 interface layer, respectively, exhibit a consistent trend with the

Figure 4. a) p-i-n device structure, b) cross-sectional SEM image of the fabricated PSC, c) J - V curve of the champion device w/o and with DTT-EHDI_2 in reverse scan under simulated AM 1.5G illumination, and d) corresponding IPCE and integrated current density. e) J - V hysteresis curve of forward and reverse scans of the PSCs. f) Stabilized initial 400 s MPP tracking of J_{SC} under ambient conditions. The statistical PV parameters of g) V_{OC} , h) J_{SC} , i) FF, and j) PCE of PSCs w/o and with DTT-EHDI_2 interface layer.

Table 1. PV parameters of the PSCs with and without **DTT-EHDI₂**.

Device ^{a)}	Scan	V _{OC} [mV]	J _{SC} [mA cm ⁻²]	FF [%]	PCE [%]	R _s [Ω]	R _{sh} [kΩ]
w/o	RS	1001.38	22.80	72.96	16.66	42.99	32.88
	FS	1008.96	22.52	70.34	15.98	45.38	28.20
	average	997.35 ± 9.8	22.58 ± 0.29	72.34 ± 0.85	16.29 ± 0.42		
with	RS	1034.09	23.18	75.71	18.15	36.05	65.96
	FS	1036.07	23.04	74.21	17.72	37.73	57.94
	average	1031.17 ± 3.9	23.06 ± 0.13	75.36 ± 0.47	17.92 ± 0.13		

^{a)}R_s and R_{sh} of PSCs were estimated by the slope of the J–V curves near V_{OC} and J_{SC}, respectively.

characteristic J–V curve (Figure 4d). We evaluated the hysteresis index (HI) following the equation $HI = [J_{RS}(0.8V_{OC}) - J_{FS}(0.8V_{OC})] / J_{RS}(0.8V_{OC})$, where $J_{RS}(0.8V_{OC})$ and $J_{FS}(0.8V_{OC})$ represent the J_{SC} at 80% of V_{OC} from reverse and forward J–V scans, respectively (Figure 4e).^[9] The molecularly engineered interface-based PSCs exhibit negligible hysteresis effect with 0.02, which is considerably lower than that of the control PSCs (0.05), suggesting the upgraded photoinduced charge transfer dynamic induced by the **DTT-EHDI₂** interfacial layer. Moreover, the PSC with **DTT-EHDI₂** interface layer showed stabilized J_{SC} (Figure 4f) at maximum power point (MPP) tracking under ambient conditions (≈40–60% RH at 28 °C). The PV statistics are presented (Figure 4g–j) and also summarized in Table 1.

To elucidate the behavior of **DTT-EHDI₂** as HTM, we fabricated inverted PSCs under the undoped conditions without NiO_x and measured 12.53% PCE (Table S1, Figure S11, Supporting Information), which is significantly higher than the reported literature with triazatruxene-based HTM in p–i–n configuration. Further, **DTT-EHDI₂** in their pristine and doped conditions as HTM in regular n–i–p configuration yielded 5.97% and 16.73%, respectively (Table S2, Figure S12, Supporting Information). The results obtained from doped **DTT-EHDI₂** under regular architecture are comparable with those of triazatruxene-based HTMs reported in other studies^[28,30] and suggest its suitability as HTL. However, we believe that the bilayer HTM formation and placement of **DTT-EHDI₂** as an interfacial layer is a simplistic approach, and material consumption is remarkably low, which is 5 and 15 times lower than that as HTM in p–i–n and n–i–p configurations, respectively. Moreover, the results obtained by placing the interfacial layer is notably high along with lower HI when compared with the results obtained as HTM in both configurations.

We further analyzed the series resistance (R_s) and shunt resistance (R_{sh}) by estimating the slope of the J–V curves near V_{OC} and J_{SC}, respectively (Table 1). The control PSC showed higher R_s of 42.99 Ω and lower R_{sh} of 32.88 kΩ, whereas the **DTT-EHDI₂** interlayer-based PSC gave notably reduced R_s of 36.05 Ω and higher R_{sh} of 65.96 kΩ values. We attribute the significantly enhanced FF for the PSC with the **DTT-EHDI₂** interface layer to the relatively reduced R_s and higher R_{sh}.^[9] The presence of a **DTT-EHDI₂** interface layer with effective electron-blocking properties and synergistically

suppressed interfacial recombination losses is responsible for the observed high R_{sh}.

We investigated the photoinduced charge transfer dynamics and recombination mechanism in PSCs with and without **DTT-EHDI₂** interfacial layer using electrochemical impedance spectroscopy (EIS) techniques in the dark. **Figure 5a** shows the Nyquist plot at 950 mV applied bias voltage in the dark which is fitted with the equivalent circuit model of R_s + R_{ctr}/CPE1 + R_{rec}/CPE2 (Figure S13, Supporting Information), where R_s, R_{ctr}, and R_{rec} represent single-series resistance, charge transfer resistance, and charge recombination resistance at the interface between perovskite/HTL, respectively.^[6,47] R_{ctr} was extracted from the high-frequency region, while R_{rec} was determined in the low-frequency region (Table 2). Two constant phase elements related to carrier diffusion in perovskite and selective layers were assigned as CPE1 and CPE2. The **DTT-EHDI₂**-based PSC featured a higher R_{rec} at the entire bias range (Figure 5b), leading to lower charge recombination and mitigated charge annihilation at the interface. The introduction of the **DTT-EHDI₂** layer reduces the energy barrier at the perovskite/HTM interface (Figure 1c), which facilitates efficient charge extraction without charge buildup at the interface, impacting V_{OC} enhancement. Moreover, at a given potential bias, the PSC incorporating **DTT-EHDI₂** shows a much lower R_{ctr} than that of the control PSC (Figure 5c). Generally, the EIS analysis is consistent with the R_s and R_{sh} obtained from the J–V curve, inferring that the **DTT-EHDI₂** interfacial layer promotes the photoinduced charge transfer dynamics at the perovskite/HTM interface.

Bode EIS spectra were conducted at 0.95 V in the dark (Figure 5d) to elucidate the impact of the **DTT-EHDI₂** interfacial layer on charge lifetime (τ), followed by $\tau = 1/(2\pi f_p)$. Here, f_p denotes the peak frequency corresponding to the electrochemical reaction of the charge transfer process at perovskite/NiO_x interface.^[48] The PSC based on the **DTT-EHDI₂** interfacial layer showed a longer charge lifetime (0.73 μs) compared with that in the PSC without the interfacial layer (0.57 μs). The enhanced electron lifetime can be credited to the reduced charge recombination, resulting in rapid charge carrier transport and enhanced electron density at NiO_x/perovskite interface. Further, τ of **DTT-EHDI₂**-based PSC is higher than that of the control PSC at various bias voltages (Figure 5e).

The J–V profile in the dark was conducted to further understand leakage current and carrier recombination behavior of the PSCs (Figure 5f). The leakage current represented by the semilogarithmic curve at the negative bias potential of the

Figure 5. a) Electrochemical impedance spectra of PSCs measured at an applied voltage of 950 mV in the dark (raw and fitted data). The potential bias-dependent b) charge transport resistance, c) interfacial charge recombination resistance extracted from Nyquist plots in the dark, d) Bode spectra of PSCs measured at an applied voltage of 950 mV in the dark, e) applied bias-dependent charge lifetime in the dark, and f) dark J - V curves for the PSCs with and without (w/o) DTT-EHDI₂.

Table 2. Extracted electrochemical parameters of the PSCs with and without DTT-EHDI₂ at 950 mV applied bias in the dark.

Device	R_{ctr} [Ω]	R_{rec} [Ω]	τ [μ s]	τ [μ s]
w/o DTT-EHDI ₂	9.02	140.70	3.58	0.57
with DTT-EHDI ₂	1.16	299.10	4.57	0.73

DTT-EHDI₂-based PSCs is much lower than that of the control PSC, signaling that the higher J_{SC} obtained is through suppressing recombination. By fitting the linear part of the curve with the Shockley equation that is given by^[6,49]

$$J_D = J_0 \left[\exp\left(\frac{V}{n_{id} K_B T}\right) - 1 \right] \quad (1)$$

where J_D is the dark current density, J_0 is the saturation current density, V is the applied voltage, q is the electron charge, K_B is the Boltzmann constant, and T is the temperature, we extracted the ideality factor (n_{id}) of the PSCs. The estimated J_0 and n_{id} for the PSCs without DTT-EHDI₂ were 9.35×10^{-6} mA cm⁻² and 3.17, respectively, whereas those for the PSCs with the DTT-EHDI₂ interface layer were 5.07×10^{-7} mA cm⁻² and 2.58, respectively. Such low J_0 and n_{id} values of the DTT-EHDI₂-incorporated PSCs indicate the efficient recombination suppression along with lower leakage current outside the depletion region upon the interfacial layer, resulting in enhanced V_{OC} , FF, and charge transfer dynamics in the fabricated PSCs.

To provide mechanistic insights into DTT-EHDI₂ impact on the photoinduced charge transfer dynamics in PSCs, we investigated the effective voltage (V_{eff})-dependent photocurrent density (J_{ph}) (Figure 6). J_{ph} and V_{eff} follow the relationships of $J_{ph} = J_L - J_D$ and $V_{eff} = V_0 - V$, respectively, where J_L is current density under illumination, J_D is current density in the dark, V_0

Figure 6. Photogenerated current density (J_{ph}) versus effective voltage (V_{eff}).

is the compensation voltage defined at $J_{ph}=0$, and V is the external bias voltage.^[6] Notably, the PSC based on **DTT-EHDI**₂ displays a rapid saturation of photocurrent at a relatively low V_{eff} of 0.207 V when compared with that of the control device (0.376 V), which we attribute to the effective charge separation and extraction behavior in the PSC on interfacial layer placement. The maximum exciton generation rate (G_{max}) is a crucial factor in PSCs, which governs the charge dissociation and collection and thus the saturation current density (J_{sat}), following the relation of $J_{sat} = eLG_{max}$ (where, e and L are elementary charges and the thickness of the perovskite layer, respectively).^[50] G_{max} of the **DTT-EHDI**₂-based PSC was calculated to be $3.62 \times 10^{21} \text{ cm}^{-3} \text{ s}^{-1}$, which is slightly higher than that of the control device with $3.55 \times 10^{21} \text{ cm}^{-3} \text{ s}^{-1}$. The enhancement in G_{max} indicates the promoted photoinduced charge generation and efficient charge transfer dynamics of the PSC on **DTT-EHDI**₂ placement.

3. Conclusion

We demonstrated a facile yet effective interface reform at NiO_x /perovskite in inverted PSCs by introducing an ultrathin layer of dopant-free organic small molecule, composed of planar triazatruxene branches with thiophene core-based semiconductor, **DTT-EHDI**₂. We noted that the placement of a thin interfacial layer improves the hole extraction ability and conductivity of NiO_x through the intermolecular charge transfer effect. **DTT-EHDI**₂ also helps in reducing the energy barrier at the interface, diminishing the possible nonradiative recombination, while promoting the photoinduced charge transfer dynamics. Interface engineering with the **DTT-EHDI**₂ boosted the device V_{OC} and FF, with an overall efficiency of up to 18.15%. Our findings offer a promising molecular interface engineering approach to fabricate dopant-free-inverted planar PSCs, which can potentially be exploited to other combinations of use of inorganic semiconductors in PVs.

4. Experimental Section

Materials: Chlorobenzene (CB, 99%), isopropanol (IPA, 99.9%), anhydrous dimethyl sulfoxide (DMSO, 99.8%), and *N,N*-dimethylformamide (DMF, 99.8%) were purchased from Acros Organics. Starting materials for perovskite were purchased from Dyesol except for PbI_2 and CsI that were procured from Tokyo Chemical Industry (TCI). [60]PCBM > 99.5% and Bathocuproine (BCP) were purchased from Solenne BV and TCI, respectively. Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.999%) and NaOH were obtained from Sigma-Aldrich. All the chemicals were purchased commercially and used without further purification.

DTT-EHDI₂ **Synthesis:** 2,6-dibromodithieno[3,2-b:2',3-d']thiophene (80 mg, 0.226 mmol), *N*-tris(2-ethylhexyl)triazatruxene boronic ester (402 mg, 0.497 mmol), K_2CO_3 (2 M, 3 mL) and $\text{Pd}(\text{PPh}_3)_4$ (26 mg, 0.02 mmol) were dissolved in THF (20 mL). The reaction mixture was stirred at reflux in the dark for 12 h, then let it be cooled down and poured into water. The organic layer was dried over MgSO_4 , concentrated, and the residue mixture was purified by column chromatography on silica gel with $\text{CH}_2\text{Cl}_2/\text{hexane} = 3:2$ as eluent to obtain the product (345 mg, $Y = 98\%$). ¹H NMR₆ (500 MHz, CDCl_3) δ (ppm): 8.25–8.3 (m, 6H), 7.88 (s, 2H), 7.5–7.7 (m, H) 7.3–7.5 (m, 10H), 4.8–5.1 (m, 12H), 2.08 (s, 6H), 0.8–1.1 (m, 84H); ¹³C NMR (125 MHz, CDCl_3) δ (ppm): 146.45, 141.42, 141.08, 141.01, 139.81, 139.34, 129.92, 128.72, 123.44, 122.42, 122.24, 119.53, 117.57, 111.48, 111.37, 108.21, 103.79, 103.54, 50.52, 38.09,

29.84, 28.26, 22.80, 13.89, 13.87, 10.13, 10.06. MS (MALDI/TOF): m/z calculated for $\text{C}_{104}\text{H}_{126}\text{N}_6\text{S}_3$: 1555.9191; found 1555.9238.

NiO_x Nanocrystals (NCs) Synthesis: NiO_x NCs were prepared based on reported procedures elsewhere, with modifications noted herein.^[25] Briefly, 25 mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 50 mL of deionized (DI) water to obtain a dark green solution. The basic pH was maintained with dropwise addition of NaOH (10 mol L^{-1}), while being stirred for 30 min. The obtained colloidal precipitation was thoroughly washed with DI water several times via ultracentrifugation and dried at 90°C overnight under vacuum. The obtained green powder was calcined for 2 h at 275°C to obtain a dark-black powder. 15 mg mL^{-1} NiO_x NC ink was prepared by dispersing the as-synthesized NiO_x NCs in DI water. The earlier solution was ultrasonicated at 45°C for 1 h and filtered using a $0.22 \mu\text{m}$ nylon filter.

Inverted Solar Cell Fabrication: FTO-coated glasses (TEC15, laser-etched) were sequentially cleaned by sonication using Hellmanex II (2 vol%) solution, deionized water, ethanol, acetone, and isopropanol and then dried by compressed airflow. The substrates were further treated by UV-ozone for 30 min before use. NiO_x film was formed atop FTO substrates by spin coating at 4000 rpm for 35 s, followed by annealing at 150°C for 30 min. The samples were transferred immediately at 100°C (to avoid moisture absorption to the samples) to the argon-filled glovebox under controlled moisture and oxygen conditions. A thin layer of **DTT-EHDI**₂ ($\approx 20 \text{ nm}$) was achieved through spin coating **DTT-EHDI**₂ in chlorobenzene (3 mg mL^{-1}) at 2000 rpm for 20 s atop NiO_x . Triple-cation-perovskite [$\text{Cs}_{0.1}(\text{FA}_{0.9}\text{MA}_{0.1})_{0.9}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$] layer was achieved according to the previous report.^[51] The PCBM solution of 15 mg mL^{-1} in chlorobenzene was spin coated at room temperature on perovskite film at 1000 rpm (500 rpm s^{-1}) for 20 s and vacuum dried for 10 min. A thin layer of BCP was deposited atop PCBM by spin coating at 5000 rpm for 40 s followed by evaporating Ag (90 nm , $<1 \text{ \AA s}^{-1}$) in a thermal evaporator under low-vacuum conditions (10^{-7} Torr). The control device was fabricated according to the earlier procedure without the interfacial layer of **DTT-EHDI**₂.

n-i-p PSCs' Fabrication: TiO_2 compact layer was deposited on precleaned and UV-ozone-treated substrates using spray pyrolysis at 500°C using 1 mL of titanium diisopropoxide bis(acetyl acetonate) precursor solution (75% in 2-propanol) in 19 mL of pure ethanol using oxygen as a carrier gas, followed by annealing for another 30 min at 500°C . TiO_2 mesoporous layer (1:8 w/v in ethanol) was spin coated on the compact layer at room temperature at 4000 rpm (2000 rpm s^{-1} acceleration) for 30 s, followed by a progressive heating step until 500°C for 30 min. The triple-cation perovskite layer was deposited similar to the p-i-n devices. 30 mM **DTT-EHDI**₂ was deposited under pristine or doped [$8.3 \mu\text{L}$ of bis(trifluoromethylsulfonyl)imide lithium salt (520 mg in 1 mL acetonitrile) and $15.1 \mu\text{L}$ of 4-*tert*-butylpyridine in 1 mL of chlorobenzene] conditions on perovskite at 3000 rpm for 20 s. For the control device, doped spiro-OMeTAD (70 mM), together with $38.4 \mu\text{L}$ of 4-*tert*-butylpyridine and $21.1 \mu\text{L}$ of bis(trifluoromethylsulfonyl)imide lithium salt [520 mg in 1 mL acetonitrile] in 1 mL of chlorobenzene was placed. Au electrode (80 nm) was thermally evaporated under pressure of 1×10^{-7} Torr.

Device and Thin-Film Characterization: Current density–voltage (J – V) curves were performed using an Oriel AAA solar simulator (Newport) producing 1 sun AM1.5G (100 mW cm^{-2}) simulating sunlight and were recorded by applying an external potential bias to the devices. The generated photocurrent was recorded at a scan rate of 100 mV s^{-1} (presweep delay: 10 s) with the help of Keithley 2400 source meter and 0.09 cm^2 black metal mask as the active area. IPCE measurements were carried out using a 150 W xenon lamp attached to a Bentham PVE300-motorized 1/4 m monochromator as the light source.

X-ray diffractograms were acquired using a D8 Advance diffractometer from Bruker (Bragg–Brentano geometry, with an X-ray tube Cu K α , $\lambda = 1.5406 \text{ \AA}$). For surface topography and phase, the images were recorded with the help of scanning probe microscopy (CSI Nano observer) and an NSG10 cantilever (NTMDT) was used; data were processed through Gwyddion software. Absorption spectra were registered with the help of a UV–vis–IR spectrophotometer (Varian Cary 50 UV/Vis

Spectrophotometer), and a Hitachi S-4800 scanning electron microscope was used to image the surface microstructure. To probe the charge extraction ability of DTT-EHDI₂, the steady-state photoluminescence (PL) was measured using Hitachi, F-7000 Fluorescence spectro-photometer, by coating a thin layer of spin-coated DTT-EHDI₂ on top of the perovskite upon quartz. It was found that the perovskite film coated with DTT-EHDI₂ showed a higher quenching in PL intensity, as illustrated in Figure S14, Supporting Information. BioLogic SP-300 impedance analyser was used to record the electrochemical impedance response.

Supporting Information

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

Acknowledgements

This work received funding from the European Union H2020 Programme under a European Research Council Consolidator grant (MOLEMAT, 726360) and PARASOL (RTI2018-102292-B-I00) and ARISE (PID2019-111774RB-I00) from the Spanish Ministry of Science and Innovation.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

charge recombination, interface engineering, NiO_x, perovskite solar cells, thiophenes

Received: September 28, 2021

Revised: December 27, 2021

Published online:

- [1] J. Jeong, M. Kim, J. Seo, H. Lu, P. Ahlawat, A. Mishra, Y. Yang, M. A. Hope, F. T. Eickemeyer, M. Kim, Y. J. Yoon, I. W. Choi, B. P. Darwich, S. J. Choi, Y. Jo, J. H. Lee, B. Walker, S. M. Zakeeruddin, L. Emsley, U. Rothlisberger, A. Hagfeldt, D. S. Kim, M. Gratzel, J. Y. Kim, *Nature* **2021**, 592, 381.
- [2] <https://www.nrel.gov/pv/cell-efficiency.html> (accessed: August, 2021).
- [3] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, 131, 6050.
- [4] D. Saranin, T. Komaricheva, L. Luchnikov, D. S. Muratov, T. S. Le, Y. Karpov, P. Gostishchev, S. Yurchuk, D. Kuznetsov, S. Didenko, A. di Carlo, *Sol. Energy Mater. Sol. Cells* **2021**, 227, 111095.
- [5] Q. Cao, Y. Li, H. Zhang, J. Yang, J. Han, T. Xu, S. Wang, Z. Wang, B. Gao, J. Zhao, X. Li, X. Ma, S. M. Zakeeruddin, W. E. I. Sha, X. Li, M. Gratzel, *Sci. Adv.* **2021**, 7, eabg0633.
- [6] N. Harindu Hemasiri, S. Kazim, S. Ahmad, *J. Mater. Chem. C* **2021**, 9, 9865.
- [7] D. Saranin, S. Pescetelli, A. Pazniak, D. Rossi, A. Liedl, A. Yakusheva, L. Luchnikov, D. Podgorny, P. Gostischev, S. Didenko, A. Tameev, D. Lizzit, M. Angelucci, R. Cimino, R. Larciprete, A. Agresti, A. di Carlo, *Nano Energy* **2021**, 82, 105771.
- [8] H. Lu, A. Krishna, S. M. Zakeeruddin, M. Gratzel, A. Hagfeldt, *iScience* **2020**, 23, 101359.
- [9] N. H. Hemasiri, S. Kazim, S. Ahmad, *Nano Energy* **2020**, 77, 105292.
- [10] Y. Du, C. Xin, W. Huang, B. Shi, Y. Ding, C. Wei, Y. Zhao, Y. Li, X. Zhang, *ACS Sustainable Chem. Eng.* **2018**, 6, 16806.
- [11] B. W. N. H. Hemasiri, J. K. Kim, J. M. Lee, *Nano-Micro Lett.* **2017**, 10, 1.
- [12] N. E. Courtier, J. M. Cave, J. M. Foster, A. B. Walker, G. Richardson, *Energy Environ. Sci.* **2019**, 12, 396.
- [13] Z. K. Wang, L. S. Liao, *Adv. Opt. Mater.* **2018**, 6, 1800276.
- [14] S. Shao, M. A. Loi, *Adv. Mater. Interfaces* **2019**, 7, 1901469.
- [15] A. Fakharuddin, L. Schmidt-Mende, G. Garcia-Belmonte, R. Jose, I. Mora-Sero, *Adv. Electron. Mater.* **2017**, 7, 1.
- [16] S. Wang, T. Sakurai, W. Wen, Y. Qi, *Adv. Mater. Interfaces* **2018**, 5, 1.
- [17] J. Chen, N. G. Park, *ACS Energy Lett.* **2020**, 5, 2742.
- [18] M. Bidikoudi, E. Kymakis, *J. Mater. Chem. C* **2019**, 7, 13680.
- [19] L. Calò, S. Kazim, M. Graetzel, S. Ahmad, *Angew. Chem., Int. Ed.* **2016**, 55, 14522.
- [20] J. Cameron, P. J. Skabara, *Mater. Horiz.* **2020**, 7, 1759.
- [21] K. M. Reza, A. Gurung, B. Bahrami, S. Mabrouk, H. Elbohy, R. Pathak, K. Chen, A. H. Chowdhury, M. T. Rahman, S. Letourneau, H. C. Yang, G. Saianand, J. W. Elam, S. B. Darling, Q. Qiao, *J. Energy Chem.* **2020**, 44, 41.
- [22] X. Xu, C. Ma, Y. Cheng, Y. M. Xie, X. Yi, B. Gautam, S. Chen, H. W. Li, C. S. Lee, F. So, S. W. Tsang, *J. Power Sources* **2017**, 360, 157.
- [23] M. B. Islam, M. Yanagida, Y. Shirai, Y. Nabetani, K. Miyano, *ACS Omega* **2017**, 2, 2291.
- [24] A. Liu, G. Liu, H. Zhu, B. Shin, E. Fortunato, R. Martins, F. Shan, *Appl. Phys. Lett.* **2016**, 108, 233506.
- [25] W. Chen, Y. Zhou, L. Wang, Y. Wu, B. Tu, B. Yu, F. Liu, H. W. Tam, G. Wang, A. B. Djurišić, L. Huang, Z. He, *Adv. Mater.* **2018**, 30, 1800515.
- [26] W. Chen, F. Z. Liu, X. Y. Feng, A. B. Djurišić, W. K. Chan, Z. B. He, *Adv. Energy Mater.* **2017**, 7, 1700722.
- [27] J. Zhou, Y. Tian, Y. Yi, Y. Wu, B. Liu, *J. Power Sources* **2021**, 506, 230102.
- [28] Y. Zhang, F. Wu, L. Chen, F. Zhang, Y. Ji, W. Shen, M. Li, Q. Guo, W. Su, R. He, *Sol. Energy Mater. Sol. Cells* **2020**, 212, 110534.
- [29] X. Liu, E. Rezaee, H. Shan, J. Xu, Y. Zhang, Y. Feng, J. Dai, Z. K. Chen, W. Huang, Z. X. Xu, *J. Mater. Chem. C* **2018**, 6, 4706.
- [30] J. Santos, J. Calbo, R. Sandoval-Torrientes, I. García-Benito, H. Kanda, I. Zimmermann, J. Aragón, M. K. Nazeeruddin, E. Ortí, N. Martín, *ACS App. Mater. Interfaces* **2021**, 13, 28214.
- [31] M. W. An, B. S. Wu, S. Wang, Z. C. Chen, Y. Su, L. L. Deng, S. H. Li, Z. A. Nan, H. R. Tian, X. L. Liu, D. Q. Yun, Q. Zhang, S. Y. Xie, L. S. Zheng, *Cell Rep. Phys. Sci.* **2021**, 2, 100662.
- [32] M. Saliba, S. Orlandi, T. Matsui, S. Aghazada, M. Cavazzini, J. P. Correa-Baena, P. Gao, R. Scopelliti, E. Mosconi, K. H. Dahmen, F. De Angelis, A. Abate, A. Hagfeldt, G. Pozzi, M. Graetzel, M. K. Nazeeruddin, *Nat. Energy* **2016**, 1, 15017.
- [33] H. Li, K. Fu, P. P. Boix, L. H. Wong, A. Hagfeldt, M. Gratzel, S. G. Mhaisalkar, A. C. Grimsdale, *ChemSusChem* **2014**, 7, 3420.
- [34] L. Calò, S. Kazim, M. Salado, I. Zimmermann, M. K. Nazeeruddin, S. Ahmad, *Sustainable Energy Fuels* **2018**, 2, 2179.
- [35] C. Igci, S. Paek, K. Rakstys, H. Kanda, N. Shibayama, V. Jankauskas, C. Roldán-Carmona, H. Kim, A. M. Asiri, M. K. Nazeeruddin, *Sol. RRL* **2020**, 4, 2000173.

- [36] L. Calió, C. Momblona, L. Gil-Escrig, S. Kazim, M. Sessolo, N. Sastre-Santos, H. J. Bolink, S. Ahmad, *Sol. Energy Mater. Sol. Cells* **2017**, 163, 237.
- [37] A. Connell, Z. Wang, Y. H. Lin, P. C. Greenwood, A. A. Wiles, E. W. Jones, L. Furnell, R. Anthony, C. P. Kershaw, G. Cooke, H. J. Snaith, P. J. Holliman, *J. Mater. Chem. C* **2019**, 7, 5235.
- [38] F. J. Ramos, K. Rakstys, S. Kazim, M. Grätzel, M. K. Nazeeruddin, S. Ahmad, *RSC Adv.* **2015**, 5, 53426.
- [39] K. Rakstys, A. Abate, M. I. Dar, P. Gao, V. Jankauskas, G. Jacopin, E. Kamarauskas, S. Kazim, S. Ahmad, M. Grätzel, M. K. Nazeeruddin, *J. Am. Chem. Soc.* **2015**, 137, 16172.
- [40] P. Y. Su, L. B. Huang, J. M. Liu, Y. F. Chen, L. M. Xiao, D. B. Kuang, M. Mayor, C. Y. Su, *J. Mater. Chem. A* **2017**, 5, 1913.
- [41] S. Wu, Z. Li, J. Zhang, T. Liu, Z. Zhu, A. K. Y. Jen, *ChemComm* **2019**, 55, 4315.
- [42] R. Li, P. Wang, B. Chen, X. Cui, Y. Ding, Y. Li, D. Zhang, Y. Zhao, X. Zhang, *ACS Energy Lett.* **2019**, 5, 79.
- [43] Q. Zhao, R. Wu, Z. Zhang, J. Xiong, Z. He, B. Fan, Z. Dai, B. Yang, X. Xue, P. Cai, S. Zhan, X. Zhang, J. Zhang, *Org. Electron.* **2019**, 71, 106.
- [44] Y. Yang, Q. Yuan, H. Li, Y. Niu, D. Han, Q. Yang, Y. Yang, S. Yi, D. Y. Zhou, L. Feng, *Org. Electron.* **2020**, 86, 105873.
- [45] H. Y. Park, D. Lim, K. D. Kim, S. Y. Jang, *J. Mater. Chem. A* **2013**, 1, 6327.
- [46] M. Tyagi, M. Tomar, V. Gupta, *J. Mater. Res.* **2013**, 28, 723.
- [47] J. Lee, S. Baik, *RSC Adv.* **2018**, 8, 1005.
- [48] J. Li, T. Jiu, C. Duan, Y. Wang, H. Zhang, H. Jian, Y. Zhao, N. Wang, C. Huang, Y. Li, *Nano Energy* **2018**, 46, 331.
- [49] N. Courtier, *Phys. Rev. Appl.* **2020**, 14, 024031.
- [50] L. Xiao, T. Liang, K. Gao, T. Lai, X. Chen, F. Liu, T. P. Russell, F. Huang, X. Peng, Y. Cao, *ACS Appl. Mater. Interfaces* **2017**, 9, 29917.
- [51] M. O. Yildirim, E. C. Gok, N. H. Hemasiri, E. Eren, S. Kazim, A. U. Oksuz, S. Ahmad, *ChemPlusChem* **2021**, 86, 785.