# Journal of Materials Chemistry C



**View Article Online** 

## PAPER

Check for updates

Cite this: J. Mater. Chem. C, 2021, 9, 3642

Received 26th December 2020, Accepted 8th February 2021

DOI: 10.1039/d0tc06049f

rsc.li/materials-c

### 1. Introduction

The organic–inorganic hybrid perovskite-based solar cell is one of the representative solar cells in photovoltaic applications and has been actively studied due to its enhanced efficiency.<sup>1,2</sup> Recently, a high efficiency of 25.2% for perovskite solar cells (PSCs) has been reported, which indicated a photovoltaic application with excellent potential values.<sup>3</sup> In PSCs, the p–i–n structure is of particular interest based on its relative ease of fabrication and hysteresis suppression effect.<sup>4–6</sup> For enhancing the application of p–i–n structured PSCs, studies to improve their efficiency and stability by modifying the active layer of the perovskite material<sup>7–10</sup> or the interlayer<sup>11–16</sup> are often conducted.

Adjusting the interlayer of the device is a simpler method for efficiency improvement. It is important to enhance the transport capacity of generated charges by modifying the hole transport layer (HTL) and the electron transport layer (ETL), as well as to reduce the resistance and trap density in the device

## Tris(4-(1-phenyl-1*H*-benzo[*d*]imidazole)phenyl)phosphine oxide for enhanced mobility and restricted traps in photovoltaic interlayers†

Jihyun Lim,‡<sup>a</sup> Do-Yeong Choi,<sup>b</sup> Woongsik Jang,<sup>a</sup> Hyeon-Ho Choi,<sup>b</sup> Yun-Hi Kim<sup>b</sup>\*<sup>c</sup> and Dong Hwan Wang<sup>\*</sup>

Among small molecule organic materials, tris(4-(1-phenyl-1*H*-benzo[*d*]imidazole)phenyl)phosphine oxide (TIPO) and 2,4,6-tris(4-(1-phenyl-1*H*-benzo[*d*]imidazol)phenyl)-1,3,5-triazine were newly synthesised and introduced into an n-type interlayer in planar perovskite solar cells for effective electron transport. The small molecule materials contain phenyl benzimidazole, which is combined with a phosphine oxide core or a triazine ring core and contributes to the improvement of charge extraction and stability. As the constituent molecules—phosphine oxide and benzimidazole—have strong polarity properties and  $\pi$ -electrons, the molecules induce passivating defects towards improving charge transport and flattening the surface morphology. Moreover, the stability of the device was increased due to the introduction of the TIPO material as the passivation and protection layer. In this electron extraction analysis, electrical resistance and surface morphology investigations were carried out *via* space charge-limited current, photoluminescence, impedance, and atomic force microscopy analyses.

structure. In particular, various attempts have been made to apply newly designed ETLs of planar PSCs by directly controlling the material to improve the electron extraction efficiency.<sup>17–19</sup> In various studies, semiconductor materials with small organic molecules have often been used as interlayers.<sup>20–24</sup> When small organic molecules are applied to a device, the performance and stability of the device usually increase through enhanced charge mobility.

Small molecule organic compounds can acquire strong chemical properties and excellent solubility by adjusting the functional groups of the molecules. Therefore, we envisage that new small molecules will improve the performance and stability of the device in the planar PSC.

We synthesise small molecules, such as bis(1-phenyl-1*H*-benzo[*d*]imidazole) phenyl-phosphine oxide (BIPO), tris(4-(1-phenyl-1*H*-benzo[*d*]imidazole)phenyl)phosphine oxide (TIPO), and 2,4,6-tris(4-(1-phenyl-1*H*-benzo[*d*]imidazol)phenyl)-1,3,5-triazine (TBIT), which are advantageous for electron extraction. Imidazole, phosphine oxide, and triazine units are well-known electron-accepting units. To compare the effect of electron extraction, we prepared BIPO, TIPO, and TBIT. Notably, BIPO was composed of a highly polar phosphine oxide core and two phenyl benzimidazole side units, while TIPO was composed of highly polar phosphine oxide core and three phenyl benzimidazole side units; TBIT had a highly electron acceptor triazine core unit and three phenyl benzimidazole side units. The core polarity and electron-accepting ability effects were systematically compared for the planar PSC.

<sup>&</sup>lt;sup>a</sup> School of Integrative Engineering, Chung-Ang University, 84 Heukseok-ro, Dongjak-gu, Seoul, 06974, Republic of Korea

<sup>&</sup>lt;sup>b</sup> Department of Materials Engineering and Convergence Technology and ERI, Gyeongsang National University, Jinju 660-701, South Korea

<sup>&</sup>lt;sup>c</sup> Department of Chemistry and RINS, Gyeongsang National University,

<sup>501</sup> Jinju-daero, Jin-ju, 52828, Republic of Korea

 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available. See DOI: 10.1039/ d0tc06049f

<sup>‡</sup> J. Lim, D.Y. Choi, and W. Jang contributed equally to this work

#### Paper

The previously reported small molecule material, BIPO, is known as an excellent electron-transporting organic material.<sup>25,26</sup> The newly designed TIPO small molecule, synthesised with the phenyl benzimidazole group in BIPO, has an electron-withdrawing property of phosphine oxide with high polarity in the core, thereby improving the electron transport.<sup>27,28</sup> Furthermore, benzimidazole (BIZ) has rich  $\pi$ -electrons with strong bases, which are expected to extract higher charges from electron donors and acceptors.<sup>29</sup> However, we synthesised another small organic molecule, a TBIT small molecule, wherein the triazine ring was substituted on the TIPO core, and the  $\pi$ -electron deficiency of the triazine ringenabled efficient extraction of charge.<sup>11</sup> These small molecules are suitable for interlayer applications based on their good solubility in isopropyl alcohol (IPA) solvents. In addition, the number of phenyl BIZ groups around the core was compared to investigate the effect of passivating Lewis acidic and basic defects of perovskite, thereby reducing the roughness of the surface when introduced into a bilaver.<sup>29</sup> Moreover, the amine group of the molecule reduces the trap density at the ([6,6]-phenyl-C71-butyric acid methyl ester) PC<sub>70</sub>BM/Ag interface and inhibits the Ag-iodide ion bonds of the perovskite, thereby contributing to the improvement in device stability. Thus, the efficiency of devices comprising a bilayer of these small organic molecules increases, and in particular, the inverted perovskite device with the TIPO interlayer applied to the PC70BM layer has been demonstrated to have a 17% increase in the power conversion efficiency (PCE) compared to the device without the interlayer.

### 2. Experimental

### 2.1. Materials

All organic synthetic reactions were performed under a nitrogen atmosphere, and the corresponding starting materials were purchased from commercial suppliers. Solvents applied to the reactions were used after drying by well-established methods. Molecule isolation was conducted *via* flash column chromatography using 230–400 mesh-sized silica gel, and the final products were purified by means of sublimation steps. For compound and device preparation, the appropriate materials, if available in the market, were obtained reasonably (Fig. S1–S9, ESI†). Also, BIPO was synthesized by the process reported in previous research of our group<sup>25,26</sup> (Scheme 1).

#### 2.2. Device fabrication

Inverted PSCs with a TIPO interlayer were fabricated as shown in Fig. 1. The device structure was indium tin oxide (ITO)sputtered glass substrate/PEDOT:PSS as HTL/MAPbI<sub>3</sub> as active layer/PC<sub>70</sub>BM as ETL/interlayer/Ag (90 nm). The glass/ITO was ultrasonically cleaned with detergent, distilled water, acetone, and IPA for at least 20 min. After cleaning, the substrates were kept in an oven (100 °C) for at least 20 min before use. The surface properties of the ITO substrate were changed to hydrophilic surfaces by UV-ozone treatment for 15 min. An HTL material of PEDOT:PSS (Al4083) was stacked on ITO by spin coating at 5000 rpm for 40 sec ( $\sim$ 40 nm). The PEDOT:PSS layer was



Scheme 1 Synthesis of BIPO, TIPO, and TBIT. Details related to the detailed synthesis method will be displayed in the ESI. $\dagger$ 

annealed at 140 °C for 10 min to remove the solvent. The CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> solution (CH<sub>3</sub>NH<sub>3</sub>I and PbI<sub>2</sub> (1.06:1 mol%)) was prepared by using a  $\gamma$ -butyrolactone (GBL) solvent and dimethyl sulfoxide in a 7:3 volume ratio, with a molar concentration of 1.4 mol  $L^{-1}$  for 12 h. The perovskite photoactive layer material was spin-coated on a PEDOT:PSS layer in one step to form a thickness of approximately 300 nm (5000 rpm and 30 s); a chlorobenzene washing solvent was used. After spin coating, the substrate was dried for 5 min on a hot plate kept at 100 °C. The PC<sub>70</sub>BM was spin-coated onto a CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> substrate with which an approximately 40 nm-thick layer was produced (2000 rpm and 40 s). Furthermore, TIPO was dispersed in IPA at a concentration of 1 mg mL $^{-1}$  using an ultrasonic processor (show Fig. S10, ESI $\dagger$ ). This solution was spin-casted on top of the PC<sub>70</sub>BM layer after the filter (10 nm or less). A 90 nm-thick Ag layer, which was employed as the cathode, was then deposited under a pressure of  $1.8 \times 10^{-6}$ Torr through thermal evaporation. All the devices were encapsulated using a resin and cover glass.

#### 2.3. Characterisation

The current density-voltage (*J*-*V*) characteristics and impedance spectra of the organic photovoltaic device were obtained using a ZIVE SP1 and a solar simulator under illuminated AM 1.5 global conditions at an intensity of 100 mW cm<sup>-2</sup> and a cell area of 0.15 cm<sup>2</sup>. The short-circuit current verification of  $J_{SC}$  related to the *J*-*V* curve was evaluated by recording the incident photocurrent efficiency spectrum of the solar cell after power calibration (ABET technologies, Inc., LS150, USA) using a monochromatic chromatograph (Dongwoo OPTRON Co., Ltd, MonoRa-500i, Korea). The surface morphology of the interlayer of PC<sub>70</sub>BM/(BIPO, TIPO, or TBIT) was observed *via* atomic force

Paper



microscopy (AFM) (Park NX10) in non-contact mode. The photoluminescence spectra were recorded *via* fluorescence spectroscopy (F-7000 fluorescence spectrophotometer, HITA-CHI, Tokyo, Japan) for determining the quenching rate of ITO/PEDOT:PSS/MAPbI<sub>3</sub>/PC<sub>70</sub>BM/(BIPO, TIPO, or TBIT). The excitation wavelength was 514 nm, while the photomultiplier voltage was 700 V. Raman spectra were obtained using a Raman microscope (Xperam200 (Nanobase.inc)) with the laser (the wavelength was 532 nm and the power was set at 5 mW). The magnification of the object lens was  $40 \times . I$  3d XPS spectra were recorded by using a KAlpha X-ray photoelectron spectrometer operating with an AleKa radiation source.

### 3. Results and discussion

The new TIPO molecule was synthesised via the nucleophilic substitution of lithiated phenyl BIZ following oxidation and compared with reported BIPO. In addition, TBIT was also newly obtained via the cyclotrimerisation of cyanophenyl BIZ. These small molecule structures were introduced as a bilayer in the inverted perovskite device, as shown in Fig. 1(a) and Fig. S11 (ESI<sup>†</sup>). In the BIPO and TIPO molecules, phosphine oxide is located in the core, which has electron-withdrawing characteristics based on high polarity. Another molecule, TBIT, has a triazine ring located at the core, which is advantageous for efficiently extracting electrons according to  $\pi$ -electron-deficient properties. The calculated dipole moments of BIPO, TIPO, and TBIT via density functional theory were compared in Fig. S12 and S13 (ESI<sup>†</sup>). The BIZ group is covalently bonded to the side of the phosphine oxide and triazine ring core, and BIPO has two, whereas TIPO and TBIT have three BIZ functional groups. The binding of BIZ groups in the molecule has a larger  $\pi$ -conjugation system according to richer  $\pi$ -electrons, which enhances the charge flow.<sup>27</sup> As the highest occupied molecular orbital (HOMO) levels of BIPO, TIPO, and TBIT are lower than that of PC<sub>70</sub>BM, the holes created in the perovskite layer are blocked (Fig. 1(b)). Therefore, when BIPO, TIPO, and TBIT molecules are applied as an interlayer between PC<sub>70</sub>BM and the electrode, they contribute to effective charge transport and suppress opposite charge movement, leading to an increased current density of the device.<sup>25,26</sup>

The structure of the synthesised TIPO, BIPO, and TBIT was confirmed *via* spectroscopy analysis. The solution  $(1 \times 10^{-5} \text{ M} \text{ using a chloroform})$  and film UV-vis absorption spectra and PL spectra of BIPO, TIPO, and TBIT are compared (Fig. 2 and Fig. S14 (ESI†)). From the UV-vis analysis of BIPO, TIPO, and TBIT, the absorption peaks were observed at 311, 312, and 342 nm in solution and 318, 315, and 349 nm in film states, respectively, which could be due to the  $\pi$ - $\pi$ \* transitions.<sup>30-32</sup> The  $\pi$ - $\pi$ \* transitions frequently appear in compounds with aromatic rings,



Fig. 2 UV-vis absorption and PL spectra of (a) TIPO and (b) TBIT with solutions and films, respectively.

#### Paper

because non-bonding and  $\pi$ -bonding electrons are largely distributed in the aromatic rings.<sup>33</sup> Thus, phenyl benzimidazole with an aromatic ring forms  $\pi$ - $\pi$ \* transitions, which are observed by the red shift of the peak (Fig. 2 and Fig. S14, ESI†). Moreover, BIPO, TIPO, and TBIT showed PL at 373, 374, and 418 nm in solution and 389, 392, and 446 nm in film states, respectively, (Table S1, ESI†). This indicates that the absorption region is more red-shifted in TIPO and TBIT than BIPO, and a larger magnitude of light absorption is achieved as the wavelength of the absorbed light becomes wider. Additionally, as it is confirmed that all of the film samples are red-shifted compared to the solution samples, the intermolecular  $\pi$ - $\pi$ \* interactions occur strongly, which improves the electron transport ability.<sup>34,35</sup>

In addition, an excellent dopant, BIZ, passivates both the Lewis acid and base defects on the surface to smoothly form the surface, thereby enhancing the performance and stability of the device.<sup>29</sup> Therefore, higher performance is expected, especially in devices with TIPO and TBIT molecules with a large number of BIZ groups. In addition, TGA of BIPO, TIPO, and TBIT materials was performed (Fig. S15, ESI†), and the detailed values of  $T_g$  of each material are shown in Table S1 (ESI†). Based on TGA analysis, the TBIT material has the best thermal stability of 188 °C.

This is because it is a molecular and structurally stable substance, which balances the N atom in the triazine with the N atom in the benzyl imidazole bound to the centre in the TBIT molecule.

Nonetheless, BIPO and TIPO are phosphine oxides with high polarity in the core, resulting in an unbalanced difference in polarity of the molecule. Notably, TIPO is more stable than BIPO by dispersing the force of the phosphine oxide attracting electrons relatively uniformly because the number of bound BIZ groups is one more TIPO than BIPO. The intramolecular stability is also demonstrated by means of thermal stability tests, where BIPO degrades at a lower temperature than TIPO.

Raman analysis was conducted to confirm the chemical bond structure of BIPO, TIPO and TBIT small molecules. As shown in Fig. 3, the Raman spectra of BIPO and TIPO showed that there is not a distinguished change owing to structural similarity. The spectra revealed two major peaks; one is assigned to P–O stretching modes from phosphine oxide, and the other is to aromatic rings and imidazole functional groups of a branch, respectively.<sup>36,37</sup> Interestingly, as the number of branches bound to phosphine oxide increased in TIPO, peaks of the branches appeared sharper than those in BIPO and downshifted from 1604 cm<sup>-1</sup> to 1602 cm<sup>-1</sup>, which indicates more  $\pi$ – $\pi$ \* stacking in the molecular structure.<sup>38</sup>

On the other hand, the Raman spectra of TBIT revealed a broad peak between 1500 and 1600 cm<sup>-1</sup> attributed to triazine rings. In particular, the peak of the branch in TBIT shifted up to 1607 cm<sup>-1</sup>. Therefore, the strong electron-withdrawing characteristics of phosphine led to the interaction with three branches, which contributed to efficient  $\pi$ - $\pi$ \* interactions in the TIPO structure.

Cyclic voltammetry (CV) measurements of BIPO, TIPO, and TBIT were performed to evaluate their electronic energy levels



Fig. 3 Raman spectrum of (a) BIPO, (b) TIPO and (c) TBIT layers.

for application in PSCs (Fig. S16 and Table S1, ESI<sup>†</sup>). The highest occupied molecular orbital (HOMO) level was calculated from the oxidation potential. The lowest unoccupied molecular orbital (LUMO) level was obtained from the HOMO level and UV-edge. As shown in Fig. 1(b), the HOMO levels of BIPO, TIPO, and TBIT are 7.07, 7.01, and 6.73 eV, respectively. Therefore, since the HOMO energy levels of the newly used small molecules are deep, they have effective hole-blocking abilities as an ETL. The effect of hole blocking and the use of organic semiconductor materials

with high electron-transporting properties enabled their use as bilayers of inverted PSC ETLs, leading to improved charge extraction.<sup>39</sup>

Fig. 4(a and b) show the *I–V* curves of the inverted perovskite device in the PC70BM/BIPO, PC70BM/TIPO, and PC70BM/TBIT interlayers. The structure of the device is ITO/PEDOT:PSS/ MAPbI<sub>3</sub>/PC<sub>70</sub>BM/(BIPO, TIPO or TBIT)/Ag, and the related photovoltaic parameters are summarized in Table 1 and Table S2 (ESI<sup>†</sup>). The highest performance of 13% is observed in the TIPO interlayer devices. The  $J_{SC}$  and fill factor (FF) values of the optimised TIPO device were 19.18 mA cm<sup>-2</sup> and 76.14%, respectively, and the current density and FF were increased by 11% and 10% compared to the pristine device. Furthermore, the increase in  $J_{SC}$  and FF parameters in the average distribution graph of the TIPO interlayer device shows excellent reliable performance (Fig. S17, ESI<sup>+</sup>). This is because the TIPO interlayer contributed to efficient charge extraction based on electron-withdrawing properties and morphology passivation. Thus, in the device with a TIPO interlayer, the current flow was accelerated and the FF was most optimised, while in the



**Fig. 4** (a) Current density–voltage (J-V) curves of devices of pristine and with BIPO, TIPO and TBIT interlayers were added onto the electron transport layer (PC<sub>70</sub>BM). (b) EQE and integrated photocurrent graphs of devices.

View Article Online

Table 1 Parameters of the device with BIPO, TIPO, and TBIT interlayers

ETL interlayer	$V_{\rm OC}$ (V)	$J_{\rm SC}~({\rm mA~cm^{-2}})$	EQE (mA $cm^{-2}$ )	FF (%)	PCE (%)
Pristine	0.927	17.25	16.35	69.17	11.07
BIPO	0.894	18.74	18.76	75.25	12.61
TIPO	0.890	19.18	19.01	76.14	13.00
TBIT	0.940	16.78	17.05	72.81	11.49

external quantum efficiency (EQE) and integrated current density analysis presented Fig. 4(b), the current density of the device was 19.01 mA cm<sup>-2</sup>, which proved an increase of 16% compared to that of the pristine device. As BIPO has weaker electron extraction properties of BIZ than TIPO, a less increased current flow occurred in the BIPO interlayer device<sup>29,40</sup> than the device with TIPO. However, the efficiency of the TBIT interlayer devices slightly increased relative to that of the pristine devices due to the amine groups of BIZ with many  $\pi$ -electrons and the core material of the triazine ring that induce electron extraction from the TBIT interlayer. Moreover, from the dark current density data (Fig. S18, ESI<sup>+</sup>), the shunt resistance of the TIPO device increased, indicating that the leakage current of the device reduced. Both the BIPO and TIPO interlayer devices have lower series resistance compared to pristine devices due to the morphology passivation effect (Table S3, ESI<sup>†</sup>).<sup>41</sup> The TBIT-based device exhibited slightly higher series resistance because TBIT is an electron- deficient triazine ring core covalently bonded to the BIZ, which improves the extraction ability of electrons, but provides reduced electron transport compared to the phosphine oxide-centred TIPO due to the difference in polarity. Accordingly, the device with the most improved performance is that with the TIPO interlayer, and the efficiency increases by 17% or more compared to the pristine device.

To confirm the morphology of the surface, AFM analysis was performed (Fig. 5). The samples for AFM analysis were prepared by forming them on the PC<sub>70</sub>BM layer to observe the morphology of the ETL. The root-mean-square (RMS) roughness values of the PC<sub>70</sub>BM/BIPO, PC<sub>70</sub>BM/TIPO and PC<sub>70</sub>BM/TBIT are 0.783, 0.631, and 1.10 nm, respectively. Compared to the roughness of the PC<sub>70</sub>BM layer (RMS value: 1.703 nm), these RMS values were reduced, which indicated the smoother surface under the electrode by forming interlayers (BIPO, TIPO, and TBIT), because the interlayers had an amorphous structure. (see Fig. S11 and S19, ESI<sup>†</sup>). The smooth morphology provides efficient passivation of the interface between PC<sub>70</sub>BM and the electrode, thereby inducing uniform electron movement and FF improvement. In particular, the PC70BM/TIPO exhibited the most reduced surface roughness, which was advantageous for higher electron extraction and collection, contributing to an FF value of over 75%. To analyse the optical characteristics of the devices, PL measurements were performed as depicted in Fig. 6. As a result of PL analysis on the ITO/PEDOT:PSS/MAPbI<sub>3</sub>/PC<sub>70</sub>BM/(BIPO, TIPO or TBIT) structure, the PL intensity of the samples with BIPO, TIPO, and TBIT materials as bilayers was reduced compared to that of the pristine sample.

This is because the electrons generated in the active layers are rapidly transported by introducing small organic molecules into the interlayer. Meanwhile, a remarkably quenched PL



Fig. 5 Topographic height atomic force microscopy (AFM) images (5  $\mu$ m × 5  $\mu$ m) of (a) ITO/PC<sub>70</sub>BM, (b) ITO/PC<sub>70</sub>BM/BIPO, (c) ITO/PC<sub>70</sub>BM/TIPO and (d) ITO/PC<sub>70</sub>BM/TBIT.

emission is observed for the  $PC_{70}BM/TIPO$ , indicating that the photoinduced electrons can be efficiently extracted by the TIPO interlayer. TIPO facilitates the separation of excitons generated in the photoactive layer, and electrons are rapidly transported and extracted based on its excellent optical properties.<sup>42</sup>

Therefore, the TIPO interlayer has phosphine oxide and amine groups of BIZ that attract electrons, thereby enhancing the efficient extraction of electrons and suppression of recombination.<sup>43</sup>

Additionally, electron-only devices were fabricated to calculate the mobility of each device (Fig. 7). An electron-only device with an ITO/ZnO/TiCl<sub>4</sub>/MAPbI<sub>3</sub>/PC<sub>70</sub>BM/(BIPO, TIPO, or TBIT)/ Ag structure was fabricated and zinc oxide was introduced as a hole-blocking layer to prevent electrons from leaking in different



Fig. 6 (a) Photoluminescence (PL) spectra (excitation at 514 nm) of devices with BIPO, TIPO, and TBIT interlayers introduced.



**Fig. 7** Space-charge-limited current (SCLC) electron mobility and trap density for electron-only devices with (a) pristine, (b) BIPO, (c) TIPO, and (d) TIBT interlayers.

directions. In addition, surface treatment of  $TiCl_4$  is required to deposit the perovskite layer on top. The *J*-*V* characteristics at a high voltage and in a dark room can be expressed according to Mott–Gurney's law:<sup>44,45</sup>

$$J_{\rm SCLC} = \frac{9}{8} \varepsilon_{\rm r} \varepsilon_0 \mu_0 \frac{V^2}{L^3}$$

where  $\varepsilon_r$  is the dielectric constant (MAPbI<sub>3</sub>),  $\varepsilon_0$  is the dielectric constant (vacuum), and L is the thickness (MAPbI<sub>3</sub>). As a result of measuring the space-charge-limited current (SCLC) device, a graph was obtained, as shown in Fig. 7, and the electron mobility of devices with the BIPO and TIPO interlayers was higher than that of the pristine device. In particular, a slightly higher electron mobility of 9.68  $\times$  10<sup>-4</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> was calculated in the device with the TIPO interlayer (Table 2). The device with the highest electron mobility by the TIPO effect has the best electronextraction properties according to the high polarity of phosphine oxide and the  $\pi$ - $\pi$  interaction effect between molecules due to the rich  $\pi$ -electrons of the BIZ and enhanced electrical conductivity,<sup>27</sup> thereby improving electron extraction.<sup>46,47</sup> The devices using BIPO and TIPO interlayers had higher electron mobility, which proved to be relatively correlated with the enhanced integrated  $J_{SC}$  and PCE (%).

The current exhibited a rapid non-linear increase, and the voltage is known as the trap-filled limit voltage ( $V_{TFL}$ ), which is

Table 2 Electron mobility and trap density factors of the pristine (pure  $PC_{70}BM$ ) device, device with  $PC_{70}BM/BIPO$ ,  $PC_{70}BM/TIPO$  and  $PC_{70}BM/$ TBIT electron transport layers

ETL interlayer	Electron mobility (cm <sup>2</sup> V <sup><math>-1</math></sup> s <sup><math>-1</math></sup> )	Trap density (cm <sup>-3</sup> )	
Pristine	$1.52 imes 10^{-4}$	$3.72 imes10^{16}$	
BIPO	$9.47 imes10^{-4}$	$2.76 imes10^{16}$	
TIPO	$9.68 imes10^{-4}$	$3.33 imes10^{16}$	
TBIT	$7.67\times10^{-4}$	$3.36\times10^{16}$	

determined from the trap state filled limit. Hence, the trap density  $(n_{\text{trap}} \text{ or } N_{\text{t}})$  can be calculated as follows:<sup>44,45</sup>

$$V_{\rm TFL} = \frac{{\rm en}_{\rm trap} L^2}{2\varepsilon_0 \varepsilon}$$

where *e* is the elementary charge,  $\varepsilon_0$  is the vacuum permittivity, and 28.8 is the relative dielectric constant of MAPbI<sub>3</sub>.<sup>48</sup> Therefore, *N<sub>t</sub>* is calculated as follows:

$$N_t = \frac{2\varepsilon_{\rm r}\varepsilon_0 V_{\rm TFL}}{eL^2}$$

In the trap density analysis, the low trap density value is calculated as  $3.33 \times 10^{16}$  cm<sup>-3</sup> for the TIPO device because the TIPO interlayer inhibits charge recombination by passing traps in the PC<sub>70</sub>BM layer. On the one hand, using the TIPO interlayer increases the current density and improves the FF of the device by efficiently transferring the charge generated in the active layer to the electrode. On the other hand, the device with the BIPO interlayer has an electron mobility value of 9.47  $\times$   $10^{-4}~\text{cm}^2~\text{V}^{-1}~\text{s}^{-1}$  , which is similar to that of the device with the TIPO, but exhibits a higher trap density, resulting in lower electron transport ability than the device with TIPO. The device with the TBIT interlayer has a relatively low electron mobility, but the trap density is  $3.36 \times 10^{16}$  cm<sup>-3</sup>, which is lower than that of the pristine device and has the effect of being passivated on the PC<sub>70</sub>BM layer, thereby eliminating traps that interfere with electron extraction under the Ag electrode. The amine groups of BIPO, TIPO, and TBIT can effectively reduce the interface trap density.49 Therefore, as the device with TIPO interlayer showed the highest electron mobility improvement and the lowest value in the trap density at the PC70BM/Ag interface, it exhibited excellent characteristics in suppressing the resistance and increasing the current density and FF,<sup>50</sup> thereby improving the performance of the PSCs. This improvement in current density suggests that the modification with TIPO reduces the injection barrier at the PC70BM/ Ag interface.

In the reflectance measurement depicted in Fig. S20 (ESI<sup>†</sup>), the low reflectance of the device with TIPO was confirmed from 350 to 400 nm, indicating that it has high light absorption compared to the absorbance data (Fig. S21, ESI<sup>†</sup>). As confirmed by PL and SCLC analyses, the electron carriers generated in the active layer were easily transported to the electrode through the TIPO interlayer. Therefore, the internal quantum efficiency (IQE) of the device was quantified to confirm the improved charge transport and extraction by introducing the TIPO interlayer. Notably, the IQE entails the calculation of the number of charge carriers extracted from the device *versus* the number of photons absorbed in the active layer. The IQE value in Fig. 8(a) is calculated as follows, through which the current flow of the device and the extraction of charge from the electrode can be confirmed.

### IQE = EQE/(1 - reflectance)

The average IQE of pristine devices shows a response of 85% at 400–750 nm, and the devices with the BIPO or TBIT interlayer showed a similar percentage response rate. However, the IQE graph of the device with the TIPO interlayer showed an average of more than 91% response from 400 to 600 nm. In particular,



Fig. 8 (a) Internal quantum efficiency (IQE) profile measurements of BIPO, TIPO and TBIT interlayers in perovskite solar cells, (b) impedance of devices with BIPO, TIPO and TBIT interlayers in the light.

the IQE response close to 98% at approximately 500 nm showed a 94% IQE current flow between 680 and 750 nm. The TIPO interlayer device with a high current density value indicated that almost all the absorbed photons were extracted and converted into a photocurrent value. The IQE value is improved by extracting the generated electrons wherein phosphine oxide,<sup>51</sup> the core of the TIPO interlayer, and strong  $\pi$ - $\pi$  stacking are formed between BIZ molecules to induce high electron mobility. The combined BIZ molecule and the phenyl group induce intermolecular charge-transfer transitions, and the electrons are effectively extracted.<sup>34,35</sup> In addition, Ag-amine bonds at the metal interface inhibit the formation of insulating Ag-I bonds on the Ag electrode surface, thereby leading to smooth electron flow inside the TIPO interlayer device.40 Therefore, improved electron mobility, excluding optical properties, was most optimized in the device with TIPO.52

Additionally, the resistances of the devices were measured through electrochemical impedance spectroscopy (EIS) analysis. The charge transport resistance exhibited upon the introduction of BIPO, TIPO, and TBIT interlayers in the light and 0 V environment was confirmed. The device with the TIPO interlayer had a reduced

View Article Online

semi-circular radius compared to the pristine device, indicating a decrease in the electron transport resistance (Fig. 8(b)). In addition, the improvement in the flow of charges is demonstrated because devices with the BIPO interlayer exhibit reduced resistance compared to the pristine device. However, TBIT exhibits a slightly reduced charge transport resistance compared to the pristine device, resulting in a higher electron transport resistance than the devices with the TIPO and BIPO interlayers, resulting in a reduced  $J_{SC}$  of the device with the TBIT interlayer. Therefore, the device with the TIPO interlayer reduces the electron transport resistance by 52% compared to the pristine device, thereby suppressing the recombination of charges and improving the electron transport. At the PC70BM/Ag interface, the high polarity properties combined with the amine groups of the TIPO molecule are due to the rapid transfer of the generated charge to the electrode before recombination. The improved electron transport capability has been demonstrated to increase the device performance by increasing the current density.<sup>52</sup>

The long-term stability of the device incorporating small molecules containing the BIZ group was predicted to be improved and verified through stability tests. The PCE decay *versus* storage time is plotted in Fig. 9. The pristine device



**Fig. 9** (a) Stability test of devices with BIPO, TIPO, and TBIT interlayers, (b) XPS analysis of the I 3d region on the surface of the structures with ITO/ PEDOT:PSS/MAPbI<sub>3</sub>/PC<sub>70</sub>BM and ITO/PEDOT:PSS/MAPbI<sub>3</sub>/PC<sub>70</sub>BM/TIPO.

showed a 100% decrease in efficiency after 24 days, and the PCE of the device with the BIPO interlayer also showed a steady decrease of 49% after 16 days. Nonetheless, the devices with TIPO and TBIT showed relatively high stability, and in particular, the former maintained excellent stability consistently for over 24 days. According to a previous report, PSC decomposition under an Ar atmosphere is mainly caused by the immigration of I<sup>-</sup> ions, which gradually corrodes the Ag cathode.<sup>53</sup> Nevertheless, it has been demonstrated that some N-containing materials might be able to capture the immigrated I<sup>-</sup> anions, thereby inhibiting the corrosion of Ag cathodes.<sup>29,40</sup> The I 3d signal was confirmed through XPS analysis on the structures of ITO/PED-OT:PSS/MAPbI<sub>3</sub>/PC70BM depending on TIPO interlayers after aging for 1 week (see Fig. 9(b)). In the structure without TIPO, the I 3d signals showed 620.3 eV and 631.9 eV peaks, which are identified as peaks of I<sup>0</sup>, not ion state, indicating the fast degradation of the pristine device.<sup>54-56</sup> On the other hand, the 618.3 eV peak observed in the structure with the TIPO interlayer indicates negatively ionized iodide  $(I^-)$ ,<sup>55,56</sup> which is related to the initial state of MAPbI<sub>3</sub>.<sup>57</sup> Thus, the I<sup>-</sup> ions were captured by the N atoms of the BIZs before reaching the electrode.<sup>29,41,56</sup> The I<sup>-</sup> peak implied that the TIPO interlayer suppressed the formation of insulating Ag-I bonds by blocking the ion migration.<sup>41</sup> Furthermore, the high stability of the device with TIPO is due to the effect of three functional groups of phenyl BIZ, and the TIPO provides an efficient passivation effect with not only the Lewis acid defects (Pb<sup>2+</sup>) but also the Lewis base defects (I<sup>-</sup>) of the perovskite device. Furthermore, the devices with TIPO and TBIT improved the stability by delaying the I<sup>-</sup> migration from the perovskite to the Ag cathode. In addition, the flat molecular shape of the TBIT makes the surface hydrophobic on the PC70BM layer, thereby suppressing the penetration of external moisture into the perovskite layer (Fig. S22, ESI†).58,59 Therefore, it was confirmed that the use of PC70BM/TIPO as the ETL has an advantage in the operational stability of the device.

### Conclusions

The improvement in the performance and stability of the devices was demonstrated by developing new small molecule materials that were advantageous for electron extraction. The TIPO, BIPO, and TBIT materials were synthesised by controlling the core and the surrounding group and compared as the interlayer of the device, respectively. The highest efficiency was confirmed in the device with TIPO, which indicated an improvement of over 17%. The introduction of a phosphine oxide core and phenyl benzimidazole induced efficient electron extraction of the ETL and enhanced electron transport of the device by forming strong  $\pi$ - $\pi$  stacking between molecules. In addition, TIPO contributed to smooth morphology and defect passivation, which were related to the improved FF and stability. The improvement of the  $J_{SC}$  and FF increased the PCE of the device, the effect of the device was verified through optical and electrical analyses, and the surface of the film was confirmed through the AFM images.

## Author contributions

J. Lim, D. Y. Choi, and W. Jang contributed equally to this work.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This research was supported by the Basic Science Research Program, through the National Research Foundation of Korea (NRF), funded by the Ministry of Science, ICT (MSIT) 2019R1A2C1087653 and 2018R1A2A1A05078734. This work was also supported by the Technology Innovation Program (no. 10062269, 'Self-assembled One-dimensional Nanofiber for High Performance Optoelectronics') funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

## Notes and references

- 1 Best Research-Cell Efficiency Chart, Photovoltaic Research, NREL; https://www.nrel.gov/pv/cell-efficiency.html.
- 2 A. Rajagopal, K. Yao and A. K. Y. Jen, *Adv. Mater.*, 2018, **30**, 1800455.
- 3 R. Wang, J. Xue, K.-L. Wang, Z.-K. Wang, Y. Luo, D. Fenning, G. Xu, S. Nuryyeva, T. Huang, Y. Zhao, J. L. Yang, J. Zhu, M. Wang, S. Tan, I. Yavuz, K. N. Houk and Y. Yang, *Science*, 2019, **366**, 1509–1513.
- 4 H. Yang, J. Zhang, C. Zhang, J. Chang, Z. Lin, D. Chen, X. Sun, H. Xi, G. Han and Y. Hao, *Sol. Energy*, 2016, **139**, 190–198.
- 5 J. You, Y. Yang, Z. Hong, T.-B. Song, L. Meng, Y. Liu, C. Jiang, H. Zhou, W.-H. Chang, G. Li and Y. Yang, *Appl. Phys. Lett.*, 2014, **105**, 183902.
- 6 F. Li, X. Deng, F. Qi, Z. Li, D. Liu, D. Shen, M. Qin, S. Wu, F. Lin, S.-H. Jang, J. Zhang, X. Lu, D. Lei, C.-S. Lee, Z. Zhu and A. K. Y. Jen, *J. Am. Chem. Soc.*, 2020, **142**, 20134–20142.
- 7 S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza and H. J. Snaith, *Science*, 2013, 342, 341–344.
- 8 W. Nie, H. Tsai, R. Asadpour, J.-C. Blancon, A. J. Neukirch, G. Gupta, J. J. Crochet, M. Chhowalla, S. Tretiak, M. A. Alam, H.-L. Wang and A. D. Mohite, *Science*, 2015, **347**, 522–525.
- 9 A. H. Slavney, R. W. Smaha, I. C. Smith, A. Jaffe, D. Umeyama and H. I. Karunadasa, *Inorg. Chem.*, 2017, 56, 46–55.
- 10 R. Fan, Y. Huang, L. Wang, L. Li, G. Zheng and H. Zhou, *Adv. Energy Mater.*, 2016, **6**, 1600460.
- 11 J. Lim, M.-S. Kim, W. Jang, D. H. Wang and J. K. Park, *Dyes Pigm.*, 2020, **178**, 108332.
- 12 W.-C. Lai, K.-W. Lin, T.-F. Guo, P. Chen and Y.-T. Wang, *Appl. Phys. Lett.*, 2015, **107**, 253301.
- 13 E. M. Sanehira, B. J. Tremolet de Villers, P. Schulz, M. O. Reese, S. Ferrere, K. Zhu, L. Y. Lin, J. J. Berry and J. M. Luther, ACS Energy Lett., 2016, 1, 38–45.

- 14 C. Ma and N.-G. Park, ACS Energy Lett., 2020, 5, 3268-3275.
- 15 Y. Liu, S. Akin, L. Pan, R. Uchida, N. Arora, J. V. Milić, A. Hinderhofer, F. Schreiber, A. R. Uhl, S. M. Zakeeruddin, A. Hagfeldt, M. I. Dar and M. Grätzel, *Sci. Adv.*, 2019, 5, eaaw2543.
- 16 H. Zhou, Q. Chen, G. Li, S. Luo, T.-B. Song, H.-S. Duan, Z. Hong, J. You, Y. Liu and Y. Yang, *Science*, 2014, 345, 542–546.
- 17 H.-L. Yip, S. K. Hau, N. S. Baek, H. Ma and A. K.-Y. Jen, *Adv. Mater.*, 2008, **20**, 2376–2382.
- 18 L.-L. Jiang, S. Cong, Y.-H. Lou, Q.-H. Yi, J.-T. Zhu, H. Ma and G.-F. Zou, *J. Mater. Chem. A*, 2016, 4, 217–222.
- 19 C. Kuang, G. Tang, T. Jiu, H. Yang, H. Liu, B. Li, W. Luo, X. Li, W. Zhang, F. Lu, J. Fang and Y. Li, *Nano Lett.*, 2015, 15, 2756–2762.
- 20 J.-S. Yeo, R. Kang, S. Lee, Y.-J. Jeon, N. Myoung, C.-L. Lee, D.-Y. Kim, J.-M. Yun, Y.-H. Seo, S.-S. Kim and S.-I. Na, *Nano Energy*, 2015, **12**, 96–104.
- 21 M. Sakomura, Y. Yokokura, Y. Takagi and K. Ueda, *AIP Adv.*, 2020, **10**, 015144.
- A. Fakharuddin, L. Schmidt-Mende, G. Garcia-Belmonte, R. Jose and I. Mora-Sero, *Adv. Energy Mater.*, 2017, 7, 1700623.
- 23 F. Wu, W. Gao, H. Yu, L. Zhu, L. Li and C. Yang, J. Mater. Chem. A, 2018, 6, 4443–4448.
- 24 L. Zhu, W. Gao, F. Wu, L. Li and C. Yang, J. Mater. Chem. A, 2018, 6, 18044–18049.
- 25 Y. R. Cheon, H.-J. Yun, K. Thangaraju and Y.-H. Kim, Synth. Met., 2014, 190, 39–43.
- 26 S.-J. Yoo, H.-J. Yun, I. Kang, K. Thangaraju, S.-K. Kwon and Y.-H. Kim, *J. Mater. Chem. C*, 2013, 1, 2217–2223.
- 27 Z. He, H. Wu and Y. Cao, Adv. Mater., 2014, 26, 1006–1024.
- 28 S. O. Jeon, K. S. Yook, B. D. Chin, Y. S. Park and J. Y. Lee, *Sol. Energy Mater. Sol. Cells*, 2010, 94, 1389–1392.
- 29 Y. Wang, Y. Yang, F. Uhlik, Z. Slanina, D. Han, Q. Yang, Q. Yuan, Y. Yang, D.-Y. Zhou and L. Feng, *Org. Electron.*, 2020, **78**, 105573.
- W. Feng, A. Fujii, M. Ozaki and K. Yoshino, *Carbon*, 2005, 43, 2501–2507.
- 31 Y.-T. Wang, Y.-S. Wu and G.-M. Tang, Opt. Mater., 2019, 98, 109432.
- 32 S. Song, S. H. Park, Y. Jin, J. Kim, J. Y. Shim, Y. Goo, O.-S. Jung, I. Kim, H. Lee, E. D. Jeong, J. S. Jin, K. Lee and H. Suh, *Synth. Met.*, 2011, **161**, 307–312.
- 33 M. Keiluweit and M. Kleber, *Environ. Sci. Technol.*, 2009, **43**, 3421–3429.
- 34 O. R. Shehab and A. M. Mansour, *J. Mol. Struct.*, 2021, **1223**, 128996.
- 35 M. J. Kamlet and R. W. Taft, *J. Chem. Soc., Perkin Trans.*, 1979, **2**, 349–356.
- 36 G. B. Deacon and J. H. S. Green, Spectrochim. Acta, Part A, 1968, 24(7), 845–852.
- 37 D. S. Caswell and T. G. Spiro, J. Am. Chem. Soc., 1986, 108(21), 6470–6477.
- 38 A. A. Profit, V. Felsen, J. Chinwong, E.-R. E. Mojica and R. Z. B. Desamero, *Proteins*, 2013, 81(4), 690–703.

### View Article Online

- 39 J. F. Butscher, Q. Sun, Y. Wu, F. Stuck, M. Hoffmann, A. Dreuw, F. Paulus, A. S. K. Hashmi, N. Tessler and Y. Vaynzof, *J. Phys. Mater.*, 2020, 3, 025002.
- 40 M. Imran, H. Coşkun, F. H. Isikgor, L. Bichen, N. A. Khan and J. Ouyang, *J. Mater. Chem. A*, 2018, **6**, 22713–22720.
- 41 H. Back, G. Kim, J. Kim, J. Kong, T. K. Kim, H. Kang, H. Kim, J. Lee, S. Lee and K. Lee, *Energy Environ. Sci.*, 2016, 9, 1258–1263.
- 42 W. Qiu, M. Buffière, G. Brammertz, U. W. Paetzold, L. Froyen, P. Heremans and D. Cheyns, *Org. Electron.*, 2015, 26, 30–35.
- 43 K. Rakstys, A. Abate, M. I. Dar, P. Gao, V. Jankauskas, G. Jacopin, E. Kamarauskas, S. Kazim, S. Ahmad, M. Grätzel and M. K. Nazeeruddin, *J. Am. Chem. Soc.*, 2015, 137, 16172–16178.
- 44 Q. Dong, Y. Fang, Y. Shao, P. Mulligan, J. Qiu, L. Cao and J. Huang, *Science*, 2015, 347, 967–970.
- 45 H. Wang, F. Yang, Y. Xiang, S. Ye, X. Peng, J. Song, J. Qu and W.-Y. Wong, *J. Mater. Chem. A*, 2019, 7, 24191–24198.
- 46 L. Duan, Y. Chen, J. Jia, X. Zong, Z. Sun, Q. Wu and S. Xue, *ACS Appl. Energy Mater.*, 2020, **3**, 1672–1683.
- 47 J. Yang, Q. Zhang, J. Xu, H. Liu, R. Qin, H. Zhai, S. Chen and M. Yuan, *Nanomaterials*, 2019, **9**, 1666.
- 48 A. Poglitsch and D. Weber, *J. Chem. Phys.*, 1987, **87**, 6373–6378.
- 49 X. Meng, C. H. Y. Ho, S. Xiao, Y. Bai, T. Zhang, C. Hu, H. Lin, Y. Yang, S. K. So and S. Yang, *Nano Energy*, 2018, **52**, 300–306.

- D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin,
   Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev,
   Y. Losovyj, X. Zhang, P. A. Dowben, O. F. Mohammed,
   E. H. Sargent and O. M. Bakr, *Science*, 2015, 347, 519–522.
- 51 Y. Zhao, C. Liang, H. Zhang, D. Li, D. Tian, G. Li, X. Jing, W. Zhang, W. Xiao, Q. Liu, F. Zhang and Z. He, *Energy Environ. Sci.*, 2015, 8, 1256–1260.
- 52 D. Yang, R. Yang, K. Wang, C. Wu, X. Zhu, J. Feng, X. Ren, G. Fang, S. Priya and S. Liu, *Nat. Commun.*, 2018, 9, 3239.
- 53 E. Bi, H. Chen, F. Xie, Y. Wu, W. Chen, Y. Su, A. Islam,
  M. Grätzel, X. Yang and L. Han, *Nat. Commun.*, 2017,
  8, 15330.
- 54 M. Sun, J. Hu, C. Zhai, M. Zhu and J. Pan, *Electrochim. Acta*, 2017, **245**, 863–871.
- 55 H. Tian, T. Gao, X. Li, X. Wang, C. Luo, X. Fan, C. Yang, L. Suo, Z. Ma, W. Han and C. Wang, *Nat. Commun.*, 2017, 8, 14083.
- 56 W. Chen, G.-n. Zhang, L.-m. Xu, R. Gu, Z.-h. Xu, H.-j. Wang and Z.-b. He, *Mater. Today Energy*, 2016, **1-2**, 1–10.
- 57 C. Rocks, V. Svrcek, P. Maguire and D. Mariotti, *J. Mater. Chem. C*, 2017, 5, 902–916.
- 58 Y. Bai, Q. Dong, Y. Shao, Y. Deng, Q. Wang, L. Shen, D. Wang, W. Wei and J. Huang, *Nat. Commun.*, 2016, 7, 12806.
- 59 Z. Zhu, D. Zhao, C.-C. Chueh, X. Shi, Z. Li and A. K. Y. Jen, *Joule*, 2018, 2, 168–183.