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# Role of LiTFSI in High T<sub>g</sub> Triphenylamine-based Hole Transporting Material in Perovskite Solar Cell

An-Na Cho,<sup>a</sup> Hui-Seon Kim,<sup>a</sup> Thanh-Tuân Bui,<sup>b</sup>\* Xavier Sallenave,<sup>b</sup> Fabrice Goubard,<sup>b</sup> Nam-Gyu Park<sup>a</sup>\*

<sup>a</sup>School of Chemical Engineering and Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Korea

<sup>b</sup>Laboratoire de Physicochimie des Polymères et des Interfaces, Université de Cergy-Pontoise, 5 mail Gay Lussac, 95000 Neuville-sur-Oise, France

\*Corresponding authors

T.-T.B.: E-mail: tbui@u-cergy.fr

N.-G.P.: E-mail: npark@skku.edu

Authors E-mail Addresses:

An-Na Cho (an.cho@skku.edu), Hui-Seon Kim (hseon.kim@skku.edu), Fabrice Goubard (fabrice.goubard@u-cergy.fr), Xavier Sallenave (xavier.sallenave@u-cergy.fr)

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## Abstract

A hole transporting material based on triphenylamine with high glass transition temperature  $(T_g)$  of 99 °C, coded as BT41, was synthesized and applied to perovskite solar cell. The pristine BT41 showed low power conversion efficiency (PCE) of 1.1% due to low photocurrent density ( $J_{sc}$ ) of ca. 6 mA/cm<sup>2</sup> and almost negligible fill factor of less than 0.2, which however significantly improved to 9.0% owing to mainly 3-times improved  $J_{sc}$  of 17.6 mA/cm<sup>2</sup> by adding both *tert*-butylpyridine (tBP) and lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) as additives. Oxidation of BT41 was dominated by LiTFSI, which is responsible for the one order of magnitude increased hole mobility. Additive addition also reduced recombination resistance, which correlates to the higher fill factor. Although both additives in BT41 contributed cooperatively to improvement of photovoltaic performance, LiTFSI played major role in the enhancement.

# Keywords: perovskite solar cell, high Tg, triphenylamine, HTM, additive, LiTFSI

# 1. Introduction

Organic-inorganic halide perovskite solar cell (PSC) has received spotlight since the report on the solid-state perovskite solar cell employing spiro-MeOTAD as a hole transporting material (HTM) in 2012<sup>1</sup> following the reports on perovskite sensitized liquid junction solar cells in 2009<sup>2</sup> and 2011.<sup>3</sup> The report on solid-state PSC in 2012 eventually triggered off researches on PSCs, as a result power conversion efficiency (PCE) reached 22.1% in 2016.<sup>4</sup>

In perovskite solar cell, needless to say, perovskite layer is most important component. However, equally important components are materials for selective contacts since selective contacts serve electron and hole extraction. TiO<sub>2</sub> has been commonly used for electron collecting, whereas various materials have been proposed as candidate for hole transporting layer. Among the proposed HTMs spiro-MeOTAD has been normally adapted for perovskite solar cell since its successful use in solid-state dye-sensitized solar cell in 1998.<sup>5</sup> Compared to polymeric HTMs, molecular HTM is beneficial to reproducibility. Nevertheless, relatively low conductivity and a highly complicated synthetic process are still issues to be addressed in

spiro-MeOTAD. A donor-acceptor type DOR3T-TBDT<sup>6</sup> and tetrathiafulvalene derivative<sup>7</sup> have been proposed as an alternative to spiro-MeOTAD because those materials demonstrated PCEs of 14.9% and 11.03%, respectively, even without additives thanks to high hole mobility.

Triphenylamine (TPA), an important constituent in spiro-MeOTAD, is regarded as basic unit for HTM. For instance, TPA linked with diphenyl led to linear  $\pi$ -conjugated small molecule showing better pore filling and efficient hole mobility.<sup>8</sup> Modification of MeOTAD structure demonstrated comparable performance for the device with spiro-MeOTAD.<sup>9</sup> Flattering of core TPA was found to increase hole transport owing to effective  $\pi$ - $\pi$  interaction, which showed PCE of 12.8% without adding additives to this HTM.<sup>10</sup>

Recently Bui et al., reported 5-(4-(bis(4-(5-(bis(4-methoxyphenyl)amino)thiophen-2yl)phenyl)amino)phenyl)-N,N-bis(4-methoxyphenyl)thiophen-2-amine (coded as BT41) based on triphenylamine core that is expected to be a candidate for HTM for perovskite solar cell because of high glass transition temperature ( $T_g = 99$  °C) allowing good contact with perovskite layer due to amorphous state.<sup>11,12</sup> In addition, BT41 is expected to be less expensive than spiro-MeOTAD because of facile synthetic process and relatively high yield. For the case of spiro-MeOTAD, its low conductivity<sup>13,14</sup> can be overcome by addition of additives such as lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) and 4-*tert*butylpyridine (tBP). Addition of both additives was found to improve significantly perovskite solar cell performance. However, the role of LiTFSI or tBP has not been clarified. In this work, effects of additives in BT41 on photovoltaic performance of perovskite solar cell are investigated. Photovoltaic performance of pristine BT41 is compared with those of BT41 including additives. BT41 with only LiTFSI is much superior to that with only tBP, which is further improved by combining two additives. Additive effects are analyzed by hole mobility, photoluminescence and impedance spectroscopy.

# 2. Experimental Section

*Synthesis of materials*. BT41 was synthesized according to the method described elsewhere.<sup>11</sup> Typical procedure: in a dry schlenk equipped with a magnetic stir bar, tris(4-(5-

bromothiophen-2-yl)phenyl)amine (628 mg, 0.8622 mmol), bis(4-methoxyphenyl)amine (890 mg, 3.88 mmol), palladium(II) acetate (19 mg, 0.08622 mmol), sodium tert-butoxide (497 mg, 5.1732 mmol), tri-tert-butylphosphine (35 mg, 0.1724 mmol, dissolved in 3 mL of dry toluene), and freshly distillated toluene (30 mL) were charged under argon stream. The mixture was then degassed by repeated vacuum evacuation/argon refill cycle (5 times) and was heated at 100°C for 80 h. After cooling to room temperature, the mixture was diluted with chloroform (100 mL) and was filtered through a short plug of silica to yield a clear vellow liquid. This solution was concentrated to give a viscous oil (ca. 3 - 4 mL) to which was added methanol (250 mL) while stirring. The precipitate was then filtered, rinsed with methanol, and dried under vacuum to yield the product as a yellow solid (787 mg, 78 % yield). <sup>1</sup>**H NMR** (DMSO-d<sub>6</sub>,  $\delta$ /ppm): 7.48 (d, 6 H, J = 8.5 Hz), 7.18 (d, 3 H, J = 3.8 Hz), 7.11 (d, 12 H, J = 9.0 Hz), 7.00 (d, 6 H, J = 8.5 Hz), 6.93 (d, 12 H, J = 9.0 Hz), 6.42 (d, 3 H, J = 4.3 Hz), 3.76 (s, 18 H). <sup>13</sup>C NMR (1,2-dichlorobenzen-d<sub>4</sub>, δ/ppm): 156.30, 152.92, 146.05, 141.66, 135.13, 122.99, 125.99, 124.90, 124.61, 121.41, 118.00, 114.82, 55.23. HRMS (ESI+): calculated for M+: 1172.3675, found 1172.3711. CH<sub>3</sub>NH<sub>3</sub>I was synthesized by reacting 27.8 ml of CH<sub>3</sub>NH<sub>2</sub> (40wt% in methanol, TCI) with 30 ml of HI (57wt% in water, Aldrich) in a round bottomed flask with vigorous stirring for 2 h in an ice bath. The precipitated CH<sub>3</sub>NH<sub>3</sub>I was collected using a rotary evaporator at 50 °C for 1 h, washed with diethyl ether four times and finally dried in vacuum for 24 h. PbI<sub>2</sub> (0.461g), CH<sub>3</sub>NH<sub>3</sub>I (0.159g) and N,N-dimethyl sulfoxide (DMSO) (0.078g) in 0.4943g of dimethylformamide (DMF) were prepared at room temperature for spin-coating of MAPbI<sub>3</sub> (MA =  $CH_3NH_3$ ) (corresponding to 52wt% solution).

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Solar cell fabrication. The compact blocking TiO<sub>2</sub> layer (bl-TiO<sub>2</sub>) was formed on the cleaned FTO glasses (Pilkington, TEC-8,  $8\Omega$ /sq) using the 0.15 M solution of titanium diisopropoxide bis(acetylacetonate) (75 wt % in 2-propanol, Aldrich) in 1-buthanol (99.8%, Aldrich) as spin coated at 2800rpm for 20s, which was followed by drying at 125 °C for 5min. The home-made nanocrystalline TiO<sub>2</sub> (diameter of about 50 nm) paste was diluted (0.1 g paste/ml 1-buthanol), which was spin-coated on the bl-TiO<sub>2</sub> at 2000 rpm for 20 s and annealed at 550 °C for 1 h to form the mesoporous TiO<sub>2</sub> (m-TiO<sub>2</sub>) layer. The m-TiO<sub>2</sub> layer was further treated with 0.02 M aqueous TiCl<sub>4</sub> (99.9%, Aldrich) solution at 70 °C for 10 min, followed by annealing at 500 °C for 30 min. The adduct method was used to prepare perovskite layer,<sup>15</sup>

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where a precursor solution containing CH<sub>3</sub>NH<sub>3</sub>I, PbI<sub>2</sub> and DMSO that were dissolved in DMF was spin-coated on the mesoporous TiO<sub>2</sub> film at 4000 rpm for 25 s and diethyl ether was dripped while spinning. The perovskite layer was formed by drying at 65 °C for 1 min and 100 °C for 9 min. BT41 was spin-coated on the top of perovskite layer at 4000 rpm for 30 s using the BT41 solutions with or without additives, where 59.04 mM BT41 was first prepared by dissolving 69.3 mg BT41 in 1 ml of chlorobenzene, to which 28.8 µl tBP (96%, Aldrich) was added and then 25 µl LiTFSI (99.95%, Aldrich) was finally added. LiTFSI solution was prepared by dissolving 520 mg LiTFSI in 1 ml acetonitrile. Finally, gold counter electrode was thermally deposited on the BT41 HTM layer at  $1 \times 10^{-6}$  torr.

Characterization. Toluene was dried by distillation from sodium metal just prior to use. NMR spectra were recorded on a Bruker DPX-250 FT-NMR spectrometer with deuterated solvent in all cases. Chemical shifts ( $\delta$ ) are given in ppm using the residual solvent signal as internal reference. High-resolution mass spectrometry was performed by the Small Molecule Mass Spectrometry platform of the CNRS IMAGIF in Gif-sur-Yvette. Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q50 TGA under argon flow at a heating rate of 20 °C/min. The temperature of thermal degradation ( $T_d$ ) was measured at the point of 5% weight loss. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q100 calorimeter, calibrated with indium and flushed with argon. Samples were scanned from -50°C to 280°C at a heating rate of 20°C/min then rapidly cooled to -50°C (quenching) and heated at the same rate to 280°C. Absorbance was measured by using a UV/Vis spectrometer (lamda35, PerkinElmer). Time-integrated photoluminescence (PL) spectra were collected using a Quantaurus-Tau compact fluorescence lifetime spectrometer (HAMAMATSU) with a 450 W CW Xenon lamp and a photomultiplier tube (PMT) detector. (Excitation wavelength 464nm, Repetition rate 10MHz) Cyclic voltammetry (CV) was measured using an Autolab (AUT128N, FRA2) electrochemical analyzer. BT41 thin film was prepared by dropping and drying the BT41 chlorobenzene solution on a glassy carbon, which was used as a working electrode, Pt and Ag/AgCl were used for a counter and a reference electrode, respectively. These three-electrode were immersed in CH<sub>2</sub>Cl<sub>2</sub> solution with 0.1 M tetrabutylammonium hexafluorophosphate (NBu<sub>4</sub>PF<sub>6</sub>) and oxidation potential was evaluated with respect to ferrocene (Fc) at a scan rate 100 mV/s. Hole mobility ( $\mu_{\rm h}$ ) was estimated from the current density (J)-voltage (V) characteristics using the space charge limited current

(SCLC) method. The Mott-Gurney equation,  $J = (9/8)\varepsilon_0\varepsilon_r\mu_h(V^2/L^3)$ , was applied to obtain  $\mu_h$ ,<sup>16</sup> where  $\varepsilon_0$  is the vacuum permittivity (8.857 x 10<sup>-12</sup> F/m),  $\varepsilon_r$  is the dielectric constant of the film ( $\varepsilon_r = 3$  was assumed<sup>17</sup>), and *L* is the thickness of the active layer. The device structure for SCLC measurement was ITO/BT41/Au and the BT41 film thickness was determined by an alpha-step IQ surface profiler system (KLA Tencor).

Photocurrent density (J)-voltage (V) was measured with a solar simulator (Oriel Sol 3 A class AAA) equipped with a 450W Xenon lamp (Newport 6279NS) and a Keithly 2400 source meter. Light intensity was adjusted with the NREL-calibrated Si solar cell having KG-2 filter for approximating one sun light intensity (100 mW/cm<sup>2</sup>). Active area was covered with aperture mask (0.125 cm<sup>2</sup>) during the measurement.

Impedance spectroscopy (IS) characterization was carried out with PGSTAT 128N (Autolab, Eco-Chemie). IS under illumination (80 mW/cm<sup>2</sup>) was measured by applying a small perturbation of AC 20 mV over a DC bias voltage with a frequency ranging from 1 MHz to 1 Hz where 1 s of equilibrium time was given between each scan. DC bias voltage ranging from 0 V to 0.7 V was applied to the device with a potential step of 0.1 V. The obtained Nyquist plots were fit using an equivalent circuit composed of a series resistance ( $R_s$ ) and two or three R-C components (resistance and capacitance in parallel) depending on the HTM composition. In high frequency region impedance raw data were fit with two R-C components in series where the sum of two resistance values represents the resistance in high frequency region ( $R_{HF}$ ). The last arc in low frequency region was fit with one R-C circuit indicating the recombination resistance ( $R_{rec}$ ).

# 3. Results and discussion

The molecular structure of BT41 is shown in **Figure 1**. Studied compound was synthesized from commercially available tris(4-bromophenyl)amine in three steps with an overall yield of 52%. Briefly, a Stille coupling between 2-tributylstannylthiophene and tris(4-bromophenyl)amine gave tris(4-(thiophen-2-yl)pheny-l)amine which was then brominated leading to tris(4-(5-bromothiophen-2-yl)phenyl)amine. The later was then subjected to threefold Pd-catalyzed Buchwald–Hartwig amination with di(4-methoxyphenyl)amine leading to BT41. The structures of intermediate and final compounds were confirmed by

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NMR and HRMS. As expected, BT41 has good solubility in common organic solvents, highly thermal stability ( $T_d = 428^{\circ}C$ ) with relative high glass transition temperature ( $T_g = 99^{\circ}C$ ).



**Figure 1.** The molecular structure of Tris(4-(5-(4,4'-dimethoxydiphenylaminyl)-2-thiophenyl)phenyl)amine (BT41)

Absorption and emission properties of BT41 are measured, where BT41 in CH<sub>2</sub>Cl<sub>2</sub> solution solution and in thin solid film are compared in **Figure 2a**. The maximum absorption appears similarly at 405 nm for the solution and 406 nm for the thin film, while the peak for the thin film is broader than that for the solution due to enhanced overlap between molecules, leading to splitting of HOMO and LUMO level.<sup>18</sup> Photoluminescence (PL) spectrum for the solution shows asymmetric single peak with maximum at 466 nm, whereas the maximum shifts to 508 nm leaving shoulder peak at 471 nm for the thin film case. The red-shift in the thin film form is related to the intermolecular  $\pi$ - $\pi$  interaction that can be enhanced by tilting triphenylamine.<sup>19</sup>

Cyclic voltammogram (CV) is measured to determine the oxidation and reduction potential of BT41.<sup>20,21</sup> **Figure 2b** shows the CV result, where oxidation potential of BT41 is determined to be -0.14 V from the onset potential. Highest occupied molecular orbital (HOMO) of BT41 is calculated to be -4.96 eV from the relation of  $E_{HOMO} = -5.1 - (E_{ox,HTM} \text{ vs. Fc/Fc}^+)$ .<sup>20</sup>



**Figure 2**. (a) Normalized absorption and photoluminescence (PL) spectra for the BT41 solution dissolved in  $CH_2Cl_2$  (black) and the BT41 film formed on plain glass (gray). (b) Cyclic voltammogram of BT41 with ferrocene as the reference (scan rate = 100mV/s).

From the combined results of optical spectroscopy and CV, HOMO and LUMO level of BT 41 are determined, which is displayed in **Figure 3** together with conduction band (CB) and valence band (VB) positions of MAPbI<sub>3</sub> and CB of TiO<sub>2</sub>. The HOMO-LUMO gap of BT41 is obtained by onset wavelength (467.9 nm) in absorption spectrum, which results in 2.65 eV. LUMO level is then estimated to be -2.31 eV from HOMO and gap energy. HOMO of BT41 is well suited for hole transfer from MAPbI<sub>3</sub>.

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![](_page_8_Figure_5.jpeg)

**Figure 3**. Energy level diagram of TiO<sub>2</sub>, MAPbI<sub>3</sub> and BT41. CB, VB, HOMO and LUMO represent conduction band, valence band, highest occupied molecular orbital and lowest unoccupied molecular orbital, respectively.

Figure 4 compares photocurrent-voltage curves of perovskite solar cells employing pristine BT41, BT41 with tBP, BT41 with LiTFSI and BT41 with both tBP and LiTFSI. The device is composed of FTO/bl-TiO<sub>2</sub>/m-TiO<sub>2</sub>/MAPbI<sub>3</sub>/BT41/Au, where thickness of m-TiO<sub>2</sub> layer and perovskite capping layer is 100 nm and 400 nm, respectively. Photovoltaic parameters are listed in Table 1. Pristine BT41 without additive shows low performance due to low photocurrent density (J<sub>sc</sub>) of 6.28 mA/cm<sup>2</sup> and almost negligible FF of 0.2. Addition of tBP to BT41 deteriorates J<sub>sc</sub> but improves V<sub>oc</sub>. J<sub>sc</sub> and FF are significantly improved to 13.25 mA/cm<sup>2</sup> and 0.48, respectively, by addition of LiTFSI, which indicates that LiTFSI dominates the enhancement of photovoltaic performance rather than tBP. Jsc is further improved to 17.64 mA/cm<sup>2</sup> and FF to 0.49 upon co-existence of tBP and LiTFSI in BT41. This indicates that although tBP itself have little impact on the performance, cooperative effect is demonstrated when tBP is combined with LiTFSI. tBP indirectly increases power conversion efficiency by enabling LiTFSI to be dissolved in the solution. Chlorobenzene is used as a solvent for BT41. Nevertheless, LiTFSI itself is insoluble in chlorobenzene due to its low polarity. tBP is required to reveal the effect of LiTFSI. PCE is significantly improved from 1.1% to 9.0% by additive effect.

![](_page_9_Figure_6.jpeg)

**Figure 4**. Current density (J)-voltage (V) curves of BT41-based perovskite solar cells depending on additives. Data are collected at reverse scan (from  $V_{oc}$  to  $J_{sc}$ ) at scan rate 200 ms (voltage settling) under 1.5G one sun illumination.

**Table1**. Photovoltaic parameters of BT41-based perovskite solar cells depending on additives.  $J_{sc}$ ,  $V_{oc}$ , FF and PCE represent short-circuit photocurrent density, open-circuit voltage, fill factor and power conversion efficiency. Data were collected at reverse scan (from  $V_{oc}$  to  $J_{sc}$ ) at scan rate of 200 ms.

PCE (%)
1.1
0.6
5.8
9.0

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Time-integrated photoluminescence (PL) is measured to investigate effect of additive on charge separation between MAPbI<sub>3</sub> and hole transport. **Figure 5** shows the normalized PL with respected to bare MAPbI<sub>3</sub>. Upon contacting MAPbI<sub>3</sub> with the pristine BT41, PL intensity is significantly reduced. PL intensity is also decreased for the MAPbI<sub>3</sub> with BT41 containing both tBP and LiTFSI, however, PL quenching is less pronounced compared to the MAPbI<sub>3</sub> with pristine BT41 without additive. This implies that additive has little effect on charge separation. The PL peaks of MAPbI<sub>3</sub> are slightly blue-shifted upon contacting BT41, which is attributed to PL of BT41. A small difference in PL quenching between the pristine BT41 and the BT41 with additives is indicative of difference in contact morphology at MAPbI<sub>3</sub>/BT41 interface.

![](_page_11_Figure_3.jpeg)

**Figure 5**. Time-integrated PL spectra for the glass/MAPbI<sub>3</sub>/PMMA (MAPbI<sub>3</sub>), the glass/MAPbI<sub>3</sub>/pristine BT41 (Pristine BT41) and the glass/MAPbI<sub>3</sub>/BT41 with tBP and LiTFSI (tBP + LiTFSI). The data are normalized with respect to the PL data for MAPbI<sub>3</sub>.

Cross-sectional scanning electron microscopy (SEM) images are compared in **Figure 6**. Pinhole-free HTM layer is formed from the pristine BT41 layer, whereas large pinholes in the HTM layer and small pinholes at interface are developed upon adding the additives to BT41. The interfacial pinholes is likely to hinder charge separation, which might be responsible for the less PL quenching for the BT41 including additives than for the pristine BT41, as observed in Figure 5. Nevertheless, better photovoltaic performance achieved after addition of additives may be related to change in carrier mobility in BT41.

![](_page_11_Figure_6.jpeg)

**Figure 6**. Cross-sectional SEM images of the full cell layout with (a) pristine BT41 and (b) BT41 with tBP and LiTFSI additives. Scale bar is 100 nm.

We have carefully examined absorption spectra of BT41 depending on additives. In **Figure 7a**, the BT41 solutions with and without additives are compared. Strong absorption at around 400 nm appears regardless of additives. The BT41 solution containing LiTFSI shows additional small peak at around 590 nm, while no addition peak appears for the BT41 with tBP. For the case of spiro-MeOTAD, a sharp peak at around 400 nm is characteristics of neutral spiro-MeOTAD and a broad peak at around 500 is newly developed due to oxidation of spiro-MeOTAD.<sup>22-25</sup> The peak appeared at longer wavelength after oxidation is due to that fact that the destabilized bonding orbital by removal of electron leads probably to decrease the transition energy. Thus, a small and broad peak at around 590 nm, which is absent in the pristine BT41, is indicative of oxidation of BT41. On the other hand, tBP does not have ability to oxidize BT41. Evolution of peak at around 590 nm is indicative of oxidation of BT41 by LiTFSI. Compared to very low performance in the presence of only tBP as observed in Figure 4, much higher photocurrent for the presence of only LiTFSI indicates strongly that oxidation of BT41 plays important role in hole conduction in HTM.<sup>26</sup>

![](_page_12_Figure_4.jpeg)

Figure 7. (a) Absorption spectra of BT41 with and without additives. Materials dissolved in chlorobenzene in glove box in argon atmosphere. Measurements were performed for the

samples aged for 80 min in air atmosphere. Inset shows absorbance in the 500-700 nm. (b) Evolution of oxidation of BT41 in the presence of LiTFSI. Absoprtion spectra were measured with chlorobenzene solution of 0.031 mM BT41 and 0.0037 mM LiTFSI every 5 min in dark at scan speed of 480 nm/min.

Space charge limited current (SCLC) is measured to estimate hole mobility. Hole only devices with ITO/BT41/Au layout are prepared for measuring SCLC.<sup>27</sup> Hole mobility is obtained by fitting the Mott-Gurney equation (see Experimental section) to the SCLC data in **Figure 8**. The film thickness was 366 nm for pristine BT41, and was 893 nm for BT41 with tBP and LiTFSI. Hole mobility of pristine BT41 is estimated to be  $3.06 \times 10^{-4} \text{ cm}^2/\text{Vs}$ , which is 20 times increased to  $7.19 \times 10^{-3} \text{ cm}^2/\text{Vs}$  upon addition of tBP and LiTFSI to BT41. Such a dramatic improvement of hole mobility correlates to oxidation of BT41 that is mainly dominated by LiTFSI. It leads to increase the hole mobility because the injected hole fills the deepest trap sites, which induces smooth potential landscape. It results in an increase of intramolecular charge transfer.<sup>22,28</sup> Along with improved hole mobility, the increased density by oxidation consequently enhances the conductivity which is proportional to the hole density and hole mobility ( $\sigma = n \times e \times \mu$ ,  $\sigma =$  electrical conductivity.<sup>13,28</sup>

![](_page_13_Figure_5.jpeg)

**Figure 8**. Current as a function of applied voltage obtained by SCLC method. HTM thickness in ITO/HTM/Au was 366 nm for pristine BT41, and 893 nm for BT41 with tBP and LiTFSI.

Impedance spectroscopy was measured to analyze the effect of additives on the resistance. Figure 9a represents Nyquist plots obtained at 0.2 V of applied voltage where solid line indicates the fit results using an equivalent circuit as described in experimental section. In Figures 9b and 9c, Nyquist plots obtained in the applied voltage ranging from 0 V to 0.7 V were used to determine the resistances as a function of bias voltage in high and low frequency range. Figure 9b shows resistance observed in high frequency region  $(R_{HF})$  which is attributed to the resistance of selective contacts such as compact TiO<sub>2</sub> and hole transport material (HTM).<sup>29,30</sup> Because the only difference between the devices was a composition of HTM where additives were artificially added to the pristine BT41, it is expected that the  $R_{HF}$ is dominantly determined by HTM layer. Moreover, it is noted that the almost biasindependent  $R_{HF}$  features are obtained, which is frequently observed when the charge transport resistance governs R<sub>HF</sub>.<sup>31</sup> As can be seen in Figure 9b, R<sub>HF</sub> of BT41 containing additives show overall lower R<sub>HF</sub> in the region of low applied voltage (0-0.4 V) compared to the pristine BT41. Therefore, the addition of additives improves charge transport in BT41 resulting in higher photocurrent density especially in the low applied voltage region where recombination process is not evident. Figure 9c represents recombination resistance  $(R_{LF})$ obtained in low frequency region. R<sub>LF</sub> was maintained constantly in low applied voltage region and began to decrease in high applied voltage region due to increased Fermi level. BT41 with additives (tBP + LiTFSI) shows higher recombination resistance compared to the pristine BT41, which is well consistent with the increased V<sub>oc</sub> for the BT41 with additives.

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![](_page_15_Figure_3.jpeg)

**Figure 9.** (a) Nyquist plots of the devices employing pristine BT41 and BT41 with additives (tBP + LiTFSI) under 0.8 sun. Nyquist plots measured at DC bias voltage of 0.2 V were shown as an example. (b) Resistances obtained in high frequency range ( $R_{HF}$ ) and (c) recombination resistance obtained in low frequency range ( $R_{LF}$ ) with respect to the applied voltage.

# Conclusions

High T<sub>g</sub> tryphenylamine based hole transporting material, BT41, was synthesized and applied to perovskite solar cell. High photovoltaic performance was hardly achieved using pristine BT41, which was however dramatically improved in the presence of tBP and LiTFSI in BT41. tBP itself had little effect but played cooperative role when combining with LiTFSI. LiTFSI played major role in oxidation of BT41 and enhancing hole mobility, which was responsible for the improved photovoltaic performance in BT41-based perovskite solar cell.

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![](_page_19_Figure_4.jpeg)

Perovskite solar cell employing triphenylamine-based HTM (BT41) showed improved photovoltaic performance in the presence of lithium salt as an additive in BT41 due to increased hole mobility by oxidation of BT41.