Hole-Transporting Polymers Containing Partially Oxygen-Bridged Triphenylamine Units and Their Application for Perovskite Solar Cells

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A series of polymers composed of partially oxygen-bridged triphenylamine units was successfully synthesized by Suzuki-Miyaura or Migita-Kosugi-Stille cross coupling reactions. In addition to the polymer with directly connected triphenylamine units, $P_1$, different π-spacers, were introduced into the polymer main chains including $m$-benzene, $P_2$, $p$-benzene, $P_3$, and bithiophene, $P_4$. Photoelectron yield spectroscopy (PYS) results showed that the highest occupied molecular orbitals of these polymers lie above the valence bands of typical metal halide perovskites, suggesting efficient hole extraction from the perovskite. When used as hole-transporting materials in perovskite solar cells, the maximum power conversion efficiency (PCE) of $P_1$–$P_4$ reached 7.9% with LiTFSI additive, while the device of $P_1$ and $P_4$ without additive showed better PCE of 12.1% and 11.1%, respectively.

Keywords: Perovskite solar cells, Hole-transporting materials, Polymer, Partially oxygen-bridged triphenylamine, Additive-free

1. Introduction

Perovskite solar cells (PSCs) have attracted considerable attention as next-generation photovoltaics over the past decade due to their high power conversion efficiencies (PCEs), solution processing, and low fabrication costs [1-4]. Cell efficiencies have increased from 3.8% to 25.2% within a remarkably short period of time [5,6], a rapid evolution in performance closely connected to the development of new hole-transporting materials (HTMs) [7,8]. To efficiently extract the photogenerated holes from the perovskite layer, the highest occupied molecular orbital (HOMO) energy level of the HTM should be closely matched to the perovskite valence band (VB). Good electrical conductivity is also desirable to transport the holes toward the counter electrode with minimal voltage drop. Finally, the hole-transporting layer should have long term chemical and structural stability under solar cell operation conditions.

Among the many compounds developed to date, a triarylamine-based organic small molecule 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD) and polymer poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) are the most commonly used in high performance PSC devices [9,10]. Both spiroOMeTAD and PTAA have low intrinsic conductivity and require chemical doping to perform effectively as the HTMs in PSCs [11-13]. Typically, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), tert-butylpyridine (TBP), and tris[2-((1H-pyrazol-1-yl)-4-tert-butylpyridine]cobalt(III)-tris[bis(trifluoromethylsulfonyl)imide] (Co(III)TFSI) are used as dopant additives to increase the conductivity of HTMs. These additives, however, are known to cause undesirable side-effects leading to the premature degradation of the solar cells [14,15]. Stable, additive-free HTMs with hole conductivities comparable with doped spiro-OMeTAD or PTAA are therefore highly desirable.

Several examples of high performance PSCs made with additive-free small-molecule HTMs have been reported [15-21]. Polymer HTMs
potentially offer more easily tunable energy levels and higher charge carrier mobility, as well as being more readily processed into thin, flat, amorphous films [22]. Polymer materials are also more suitable for industrial-scale, large area fabrication. Despite these attractive features, polymeric HTMs have received comparatively little attention [13,22-31].

We have recently developed an original π-conjugated skeleton in which three phenyl groups are constrained in a quasiplanar fashion by two oxygen bridges [32-38]. The more planar geometry compared to the propeller-like triarylamines is desirable as it facilitates π-conjugation over the entire skeleton. We have thoroughly reported the effectiveness of this quasiplanar triarylamine structure in small molecular HTMs for both PSC [35,37] and OLED devices [38].

In the present study, the partially oxygen-bridged triphenylamine is built into a series of new conjugated polymers, either connected directly (P1), or coupled through m-benzene (P2), p-benzene (P3) or bithiophene (P4) π-spacers (Fig. 1). These HTMs were successfully synthesized by Suzuki-Miyaura or Migita-Kosugi-Stille cross coupling reactions. The enhanced planarity of the partially bridged triarylamines in the polymer backbone leads to more effective conjugation along the polymer chain. PSCs were fabricated using these polymers as HTMs, with and without additives. The device efficiency using P1 and P4 without additives reached 12.1% and 11.1%, respectively.

2. Experimental

2.1. Materials

All reagents were purchased from commercial sources and used without further purification. Solvents were dried and purified using standard techniques.

2.2. General methods

All reactions were carried out under argon atmosphere. TLC was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed by using PSQ 60B (Fuji Silysia). 1H NMR spectra were recorded on JEOL ECA 500 spectrometer (500 MHz for 1H NMR). The NMR chemical shifts are reported in ppm relative to the residual protons of CDCl3 (δ = 7.26 ppm) or benzene-d6 (δ = 7.16 ppm).

Analytical GPC was performed on an HLC 8120 GPC system with a TOSOH TSKgel GMHR-H(S)HT column. o-Dichlorobenzene was used as the eluent with a flow rate of 1.0 mL min⁻¹ at 140 °C. The columns were calibrated against nine standard polystyrene samples (Mn = 1200–141000).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was performed on a Shimadzu TGA-50 apparatus and Shimadzu DSC-60 apparatus (Shimadzu Co.), respectively.

UV-vis absorption measurements were performed with a Shimadzu UV-3150 spectrometer (Shimadzu Co.), in degassed spectral grade solvents.

The HOMO energy levels in the solid state were determined from the onset of photoelectron spectra measured by photoelectron yield spectroscopy (PYS) under vacuum, model BIP-KV201 (accuracy: ±0.02 eV, extraction voltage = 10 V) (BUNKOUKEIKI Co., Ltd.)

Atomic force microscopy images were taken with a Molecular Imaging Picoplus operating in AC-mode, with Nanoworld NCSTR soft tapping mode tips. SEM images were recorded with a Hitachi High-Technologies Co. SU8010.

Photocurrent-voltage measurements for perovskite solar cells were obtained in air with an OTENTO-SUNIII (BUNKOUKEIKI Co., Ltd.) solar simulator and a Keithley 2400 source meter. The light intensity of the illumination source were adjusted by using standard silicon photodiodes: BS520 for J-V characteristics and SiPD S1337-1010BQ for IPCE measurements.

Geometry optimization and DFT calculations were performed using Gaussian 09 (revision A.02) software [40].

2.3. Synthesis

2.3.1. Synthesis of compound 2

2-Decyl-1-tetradecanol (42.5 g, 120 mmol) and PPh3 (37.7 g, 144 mmol) were dissolved in CH2Cl2 (150 mL), and the solution was cooled down to 0 °C. To that solution, N-bromosuccinimide (NBS) (25.6
g, 144 mmol) was added in small portions. The reaction solution was then stirred at room temperature for 6 h. After removal of CH₂Cl₂, the residue was washed with hexane and filtered. The filtrate was concentrated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (hexane, Rₜ = 0.76) to give 48.2 g of 2 (115 mmol, 96% yield) as colorless oil.

³¹H NMR (500 MHz, CDCl₃): δ 3.45–3.44 (d, 2H), 1.60 (t, 1H), 1.27 (m, 40H), 0.89 (t, 6H).

2.3.2. Synthesis of compound 3
In a dry two-neck flask, magnesium (0.51 g, 21.3 mmol) was initially treated with iodine (0.08 g, 0.63 mmol), 12 mL of dry THF and 2 (7.11 g, 17.1 mmol) were carefully added, and the resulting mixture was refluxed at 70 °C for 6 h. Then the Grignard reagent was transferred via cannula to a solution of monobromo intermediate 1 (3.00 g, 8.52 mmol) and Pd(dppf)Cl₂ (0.35 g, 0.42 mmol) in 30 mL of dry THF. The reaction solution was further stirred for 48 h at 60 °C. The reaction mixture was then cooled down to room temperature, quenched by 10 mL of 1.0 M HCl solution, and extracted by CH₂Cl₂. The organic layer was dried over Na₂SO₄, and then the filtrate was concentrated under reduced pressure to give polymer as a yellow solid (458 mg, 40% yield).

³¹H NMR (500 MHz, benzene-d₆): δ 6.94 (s, 2H), 6.73–6.71 (d, 2H), 6.51–6.50 (d, 2H), 6.35 (s, 2H), 2.30–2.29 (d, 2H), 1.58 (s, 1H), 1.33 (m, 40H), 0.94–0.91 (t, 6H).

2.3.3. Synthesis of compound 4
In a dry two-neck flask, 3 (2.00 g, 3.28 mmol) was dissolved in CH₂Cl₂ (10 mL). To that solution, a solution of N-bromosuccinimide (NBS) (1.29 g, 7.22 mmol) in CH₂Cl₂ (30 mL) was added dropwise. The reaction mixture was stirred at room temperature overnight under argon atmosphere and dark condition. The reaction mixture was poured into water and extracted with CH₂Cl₂. The organic layer was separated, dried over Na₂SO₄ and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane, Rₜ = 0.64) to give 0.89 g of 4 (1.0 mmol, 40% yield) as colorless oil.

³¹H NMR (500 MHz, benzene-d₆): δ 7.78 (s, 2H), 7.62–7.60 (d, 2H), 7.12–7.10 (d, 2H), 6.36 (s, 2H), 2.27–2.25 (d, 2H), 1.55 (s, 1H), 1.33–1.31 (m, 40H), 1.13 (m, 24H), 0.94 (t, 6H).

2.3.4. Synthesis of compound 5
In a dry two-neck flask, 4 (2.00 g, 2.61 mmol) was dissolved in dry THF (50 mL). The solution was cooled down to −78 °C. To that solution, n-butyl lithium (2.35 mL, 5.73 mmol, 2.44 M in hexane) was added dropwise. The solution was stirred for further 1 h at −78 °C, then 2-isopropoxy-4,5,5-tetramethyl-1,3,2-dioxaborolane (2.13 mL, 10.4 mmol) was slowly added by syringe. The mixture was slowly warmed up to room temperature and left stirring overnight. The crude product was quenched by sat. NH₄Cl aqueous solution, extracted with ethyl acetate and washed with brine. The organic layer was dried over Na₂SO₄, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane:ethyl acetate, 9:1, Rₜ = 0.43) to give 0.89 g of 5 (1.0 mmol, 40% yield) as colorless oil.

³¹H NMR (500 MHz, benzene-d₆): δ 7.88 (s, 3H), 7.62–7.60 (d, 2H), 7.12–7.10 (d, 2H), 6.36 (s, 2H), 2.27–2.25 (d, 2H), 1.55 (s, 1H), 1.33–1.31 (m, 40H), 1.13 (m, 24H), 0.94 (t, 6H).

2.3.5. Synthesis of P1
K₂PO₄ (1.59 g, 7.53 mmol), Pd₂dba₃-CHCl₃ (9.75 mg, 9.42 µmol) and P(o-toly)₃ (17.2 mg, 56.5 µmol) were added to a toluene/1,4-dioxane/water (2:1:1, v:v:v) solution (12 mL) of 4 (0.72 g, 0.94 mmol) and 5 (0.81 g, 0.94 mmol) in argon. The reaction mixture was deoxidized by bubbling with dry argon for 1 h. The solution was refluxed for 24 h at 120 °C. After the reaction, the solution was cooled down to room temperature and poured into methanol to precipitate the polymer. The polymer was purified by successive Soxhlet extraction using methanol, acetone, and CHCl₃. After evaporating CHCl₃, the polymer was further purified by flash silica gel column chromatography using toluene as the eluent, and the solution was concentrated and dried under reduced pressure to give polymer as a yellow solid (458 mg, 40% yield).

2.3.6. Synthesis of P2
K₂PO₄ (0.22 g, 1.04 mmol), Pd₂dba₃-CHCl₃ (2.69 mg, 2.60 µmol) and P(o-toly)₃ (4.75 mg, 15.6 µmol) were added to a toluene/1,4-dioxane/water (2:1:1, v:v:v) solution (20 mL) of 4 (0.20 g, 0.26 mmol) and 1,3-benzenediboronic acid bis(pinacol) ester (86.0 mg, 0.26 mmol) in argon. The reaction mixture was deoxidized by bubbling with dry argon for 1 h. The solution was refluxed for 48 h at 110 °C. After the reaction, the solution was cooled down to
room temperature and poured into methanol to precipitate the polymer. The polymer was purified by successive Soxhlet extraction using methanol, acetone, and CHCl₃. After evaporating CHCl₃, the polymer was further purified by flash silica gel column chromatography using toluene as the eluent, and the solution was concentrated and dried under reduced pressure to give polymer as a yellow solid (130 mg, 75% yield).

2.3.7. Synthesis of P₃
K₂PO₄ (0.22 g, 1.04 mmol), Pd₂dba₃·CHCl₃ (2.69 mg, 2.60 μmol) and P(o-tolyl)₃ (4.75 mg, 15.6 μmol) were added to a toluene/1,4-dioxane/water (2:1:1, v:v:v) solution (20 mL) of 4 (0.20 g, 0.26 mmol) and 1,4-benzenediboronic acid bis(pinacol) ester (86.0 mg, 0.26 mmol) in argon. The reaction mixture was deoxidized by bubbling with dry argon for 1 h. The solution was refluxed for 24 h at 110 °C. After the reaction, the solution was cooled down to room temperature and poured into methanol to precipitate the polymer. The polymer was purified by successive Soxhlet extraction using methanol, acetone, and CHCl₃. After evaporating CHCl₃, the polymer was further purified by flash silica gel column chromatography using toluene as the eluent, and the solution was concentrated and dried under reduced pressure to give polymer as a yellow solid (165 mg, 92% yield).

2.3.8. Synthesis of P₄
Pd₂dba₃·CHCl₃ (2.02 mg, 1.95 mmol) and P(o-tolyl)₃ (2.37 mg, 7.78 mmol) were added to a toluene solution (5 mL) of 4 (0.15 g, 0.20 mmol) and 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (96.0 mg, 0.20 mmol) in argon. The reaction mixture was deoxidized by bubbling with dry argon for 1 h. The solution was refluxed for 24 h at 110 °C. After the reaction, the solution was cooled down to room temperature and poured into methanol to precipitate the polymer. The polymer was purified by successive Soxhlet extraction using methanol, acetone, and chlorobenzene. After removal of chlorobenzene, the polymer was further purified by flash silica gel column chromatography.
using toluene as the eluent, the solution was concentrated and dried under reduced pressure to give polymer as a dark red solid (141 mg, 94% yield).

2.4. Device fabrication
A compact TiO$_2$ layer (~40 nm) was prepared on top of UV-ozone cleaned FTO-coated glass substrate (sheet resistance of 12 Ω per square, 25 mm × 25 mm, Asahi Glass Co., Ltd., Japan) by spray-pyrolysis at 450 °C using a diluted titanium disopropoxide bis(acetylatedonate) solution (75 wt% in 2-propanol) in ethanol (1:39, volume ratio). The compact TiO$_2$ layer was treated with aqueous TiCl$_4$ (4.4 μL mL$^{-1}$) at 70 °C for 30 min, washed with deionized water and sintered at 500 °C for 20 min. A mesoporous TiO$_2$ was prepared on top of compact TiO$_2$ layer by spin-coating at 5000 rpm using a diluted commercially available precursor paste (PST-18NR) in ethanol (1:5, weight ratio). The perovskite films were prepared from CH$_3$NH$_3$PbI$_3$ stock solution (1.1 M in DMSO) [41]. The substrate was first spun at 1000 rpm for 40 s by a slope of 1s, waited for 30 s at 0 rpm, and then spun at 5000 rpm by a slope of 5 s. During the spin-coating after 92 s, 0.5 mL of anhydrous toluene was carefully dropped onto the substrate till the substrate become transparent. The resulting colorless films were dried at 50 °C for 5 min followed by annealed at 100 °C for 30 min. The hole-transporting layer was deposited on the perovskite layer by spin-coating at 3000 rpm for 30 s from respective polymer solutions in anhydrous chlorobenzene (10 mg mL$^{-1}$) which containing 4 μL of 4-tert-butylpyridine and 1.02 mg of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). After hole-transporting layer deposition the substrates were annealed at 70 °C for 30 min. Finally, 80 nm of gold was thermally evaporated on top of the active layer under high vacuum (2.5 × 10$^{-4}$ Pa).

3. Results and discussion
3.1. Synthesis
The synthetic routes to the target polymers are shown in Scheme 1. Monobromo intermediate I and 2-decyltetradecyl bromide 2 were synthesized according to previously reported procedures [33,39]. 2-Decyltetradecylmagnesium bromide Grignard reagent was prepared from 2-decyltetradecyl bromide 2 and was converted to 3 by Kumada-Tamao coupling reaction. In the next step, the key compound 4 was synthesized in 98% yield by dibromination of 3. Compound 5 was synthesized by lithiation of 4 with isopropoxyboronic acid pinacol ester in 40% yield. Finally, P1–P4 were synthesized by using either Suzuki-Miyaura (P1–P3) or Migita-Kosugi-Stille (P4) coupling polymerization between 4 and corresponding π-sparers.

The resulting polymers were separated from the residual catalyst and low molecular weight impurities by precipitation in methanol and successive Soxhlet extraction with methanol, acetone, and CHCl$_3$ or chlorobenzene. P1, P2, P3, and P4 were obtained in 40%, 75%, 92%, and 94% yield, respectively. All the polymers show good solubility in common organic solvents, such as CHCl$_3$, toluene, THF, or chlorobenzene.

The molecular weights of the polymers were determined by gel permeation chromatography (GPC) method using polystyrene as standard and o-dichlorobenzene as the eluent at 140 °C. The GPC data were summarized in Table 1. The number-average molecular weights ($M_n$) of the polymers were 10500, 16500, 33800 and 13300 g mol$^{-1}$, with a polydispersity index (PDI) of 1.5, 1.6, 2.0 and 1.3 for P1, P2, P3, and P4, respectively.

| Polymer | $M_n$ (g mol$^{-1}$) $^a$ | PDI $^a$ |
|---------|------------------------|--------|
| P1      | 10500                  | 1.5    |
| P2      | 16500                  | 1.6    |
| P3      | 33800                  | 2.0    |
| P4      | 13300                  | 1.3    |

$^a$ Determined by GPC in o-dichlorobenzene at 140 °C using polystyrene standard.

3.2. Thermal properties
Thermogravimetric (TGA) and differential scanning calorimetry (DSC) measurements were carried out to investigate the thermal properties of target polymers.

As shown in Fig. 2a, the decomposition temperature for 5% weight loss ($T_{\text{d}}$) of P1, P2, P3, and P4 were estimated to be 402, 412, 404, and 384 °C, respectively, suggesting their good thermal stability. The high thermal stability is beneficial to the long-term durability of PSCs.

From the DSC results (Fig. 2b), the glass transition temperature ($T_g$) of P1, P3, P4, and PTAA was estimated to be 76 °C, 73 °C, 73 °C, and 73 °C, respectively. No glass transition could be observed in the case of P2, and all the DSC curves were otherwise featureless. We can therefore expect that kept below $T_g$ the polymers are amorphous. The thermal stability, while less than ideal, is closely
comparable to PTAA. Increasing the $T_g$ is a key goal in the future development of these polymeric HTMs.

Fig. 2. (a) TGA thermograms at a heating rate of 10 °C min$^{-1}$ and (b) DSC curves for P1–P4 and PTAA at a heating rate of 2 °C min$^{-1}$. Measurements made under N$_2$ atmosphere.

The amorphous nature of the polymer thin films was also confirmed by two-dimensional grazing incidence X-ray diffraction (2D-GIXD). The films were prepared by spin-coating the corresponding chlorobenzene solution of polymers (20 mg mL$^{-1}$) on ITO substrates. Except for the halo corresponding to ITO substrate, no diffraction peaks were resolved for P1–P4 or PTAA (Fig. 3).

![2D-GIXD images of PTAA and P1–P4 thin films on ITO substrates.](image)

Fig. 3. 2D-GIXD images of PTAA and P1–P4 thin films on ITO substrates.

3.3. Photophysical properties

The normalized UV-vis absorption spectra of P1–P4 and PTAA thin films are shown in Fig. 4. The films were prepared by spin-coating the corresponding chlorobenzene solution of polymers (20 mg mL$^{-1}$) on quartz substrates. The absorption data together with the optical band gaps are summarized in Table 2.

![Normalized UV-vis spectra of P1–P4 thin films.](image)

Fig. 4. Normalized UV-vis spectra of P1–P4 thin films.

| Polymer | $\lambda_{\text{max}}$ (nm) | $\lambda_{\text{edge}}$ (nm) | $E_{\text{opt}}$ (eV) |
|---------|-----------------|-----------------|-----------------|
| P1      | 439             | 480             | 2.58            |
| P2      | 405             | 436             | 2.84            |
| P3      | 434             | 470             | 2.64            |
| P4      | 504             | 548             | 2.26            |
| PTAA    | 394             | 417             | 2.97            |

* Determined by using following equation, $E_{\text{opt}} = 1240/\lambda_{\text{edge}}$.

Among four polymers, P2 shows the most blue-shifted absorption due to the disconnection in π-conjugation that stems from $m$-benzene spacers between two quasiplanar units [35]. In contrast, P4, which contains bithiophene groups as spacers possesses higher planarity than the others, shows the most red-shifted absorption band. The optical bandgaps ($E_{\text{opt}}$) of these polymers, derived from the absorption edges, are 2.58, 2.84, 2.64, and 2.26 eV for P1, P2, P3, and P4, respectively.

Density functional theory (DFT) calculations at
the B3LYP-6/31G(d) level of theory were conducted for tetramer model compounds PTAA’ and P1’–P4’ [40]. As shown in Fig. 5, the oxygen-bridged triarylamine units in P1’–P4’ showed higher planarity compared to the twisted structure of PTAA’. The dihedral angle between the thiophene spacer and the triphenylamine structure in P4’ was 22°, smaller than the dihedral angles between two adjacent phenyl groups in PTAA’ and P1’–P3’ (nearly 35°), suggesting a more planar configuration for P4’. It is worth noting that, while the HOMOs of P2’ and P3’ are mainly localized on quasi-planar triphenylamine units, that of P4’ delocalizes through the bithiophene spacers. This may be ascribed to the higher planarity of P4’ as well as the more electron-donating nature of the bithiophene spacers.

Fig. 5. Optimized molecular geometries, depictions of frontier orbitals, and Kohn-Sham energy levels of tetramer model compounds P1’–P4’ and PTAA’ with ethyl groups as side chains. DFT calculations were performed at the B3LYP-6/31G(d) level of theory.

3.4. Electronic properties
The HOMO energy levels (E_HOMO) of P1, P2, P3, P4, and PTAA thin films were estimated from surface ionization potentials (IPs) measured by the photoelectron yield spectroscopy (PYS) under vacuum (Fig. 6). The HOMO energy level of P1 (–5.07 eV) and P4 (–5.16 eV) were higher than that of PTAA (–5.21 eV), while those of P2 (–5.44 eV) and P3 (–5.32 eV) were lower. The lower HOMO energies of P2 and P3 are most likely due to the ineffective expansion of orbitals through the π-spacers.

Fig. 6. PYS spectra of the thin film of PTAA and P1–P4 under vacuum.

The LUMO energy levels of polymers were estimated by using the following equation: E_LUMO = E_HOMO + E_opt. The electrochemical data and the frontier orbital energy levels of these polymers are summarized in Fig. 7, together with the conduction and valence band energies of the model perovskite CH3NH3PbI3. The HOMO and LUMO energy levels of the polymer thin films lie above both the valence band (VB, –5.45 eV) and conduction band (CB, –3.95 eV) of CH3NH3PbI3. These polymers are therefore not only expected to work well as HTMs but also to serve as electron blocking material to prevent charge recombination.

Fig. 7. Frontier orbital energy levels of P1–P4.

*aEstimated from PYS spectra. bE_LUMO = E_HOMO + E_opt.
3.5. Hole-transporting properties

Space charge limited current (SCLC) measurements were made on hole-only devices to estimate the charge carrier mobility [36] (Fig. 8). The device structure was ITO (indium tin oxide)/PEDOT: PSS (poly(3,4-ethylenedioxythiophene):polystyrene sulfonate)/[P1, P2, P3, P4 or PTAA]/Au.

![Fig. 8. SCLC measurements on hole-only devices.](image)

The hole mobility of P1 and P4 was found to be $2.8 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ and $2.6 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively, slightly higher than that of PTAA ($2.0 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$). In contrast, the hole mobility of P2 ($1.5 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$) and P3 ($3.4 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$) are about one order of magnitude lower than those of the other polymers. This is attributed to the better delocalization of the HOMOs of P1 and P4, enhancing the hole transfer integral, as mentioned in DFT calculations part.

3.6. Device fabrication and photovoltaic properties

P1–P4 were used as HTMs in regular-type, mesoporous PSCs. For comparison, reference devices with PTAA were also fabricated [41-43]. The device structure was FTO/compact TiO$_2$ (c-TiO$_2$)/mesoporous TiO$_2$ (mp-TiO$_2$)/CH$_3$NH$_3$PbI$_3$/[HTM]/Au.

The morphology of P1–P4 thin films spin coated on perovskite was confirmed by AFM. The results are summarized in Fig. 9. Generally, the polymer films conformed to the morphology of the perovskite underlayer, with only a small reduction in surface roughness due to filling up depressions and cracks in the underlayer. The surfaces of the polymers with additives are uniformly smoother than the additive-free materials. Only one film, P4 with additive, showed a distinct morphology change due to non-uniform aggregation of the polymer. In all cases the coverage appears uniform. Cross-sectional SEM images are shown in Fig. 10, from which the thickness of the perovskite layers and hole-transporting layers were estimated to be 200-300 nm and 40-60 nm, respectively. The current density-voltage ($J-V$) curves are shown in Fig. 11, and the photovoltaic parameters derived from the $J-V$ measurements are summarized in Tables 3 and 4.

As shown in Table 3 and Fig. 11a, the devices using the polymers (P1–P4) with additives (LiTFSI) resulted in poor performance with PCEs lower than 8%, due to low short circuit current densities ($J_{SC}$) and fill factors (FF). The TBP/LiTFSI additives, which effectively dope PTAA, are clearly not suitable for polymers (P1–P4). Though the cause of this incompatibility is not known, similar findings have been reported elsewhere [15,18].

![Fig. 9. Morphology of the polymer films P1–P4 and PTAA, with and without additives, spin-coated on a perovskite layer. The bare perovskite surface is shown for reference. Scans are 3 μm x 3 μm, the z-axis color scale is fixed at 160 nm (black-white) for all images.](image)
Fig. 10. Cross-sectional SEM images perovskite solar cells.

Fig. 11. $J$–$V$ characteristics of the P1–P4 and PTAA-based PSCs (a) with and (b) without additives with an active area of 0.1 cm$^2$ under a photon flux of 100 mW cm$^{-2}$ (AM1.5G) in forward scan.

Table 3. Photovoltaic parameters of P1–P4 and PTAA-based PSCs prepared with additives, derived from forward $J$–$V$ scans. The values for the champion device are shown, with the average value and standard deviation (±1σ) given in parenthesis.
The reference device prepared from PTAA with additive showed PCE of 17.6%. When the devices were fabricated without any additives (Table 4 and Fig. 11b), the PCE of PTAA decreased to 4.8%, and that of P2 resulted in 1.3% PCE. In contrast to PTAA and P2, the PCEs of devices using P1, P3, and P4 significantly increased to 12.1%, 9.1%, and 11.1%, respectively, accompanied with their improvement of JSC.

The JSC for the PSCs using P1, P2, P3, P4 and PTAA are 21.6 mA cm⁻², 11.3 mA cm⁻², 20.6 mA cm⁻², 21.6 mA cm⁻², 19.8 mA cm⁻², respectively. The upward trend in JSC (P2 << P3 < P1 ≈ P4) corresponds closely to the tendency in hole mobility.

The FF is known to be correlated with the series resistance (Rs) of solar cells. The lower FF value of the device using P2 (0.14) and PTAA (0.25) compared to those of devices using P1 (0.54), P3 (0.45) and P4 (0.50) can be attributed to the higher Rs of P2 (469.6 Ω cm²) and PTAA (170.0 Ω cm²) compared to those of P1 (16.3 Ω cm²), P3 (35.3 Ω cm²) and P4 (19.1 Ω cm²).

Except P2, the other HTMs showed comparable open circuit voltage (VOC) in the range of 0.97 V (P3, PTAA) to 1.04 V (P1 and P4). The low VOC of P2 (0.83 V) is most likely due to its lower HOMO level (−5.44 eV) close to VB of CH3NH3PbI3 perovskite (−5.45 eV), suggesting the importance of energy level matching (≈ +0.1 eV) [35] in the molecular design of polymer HTMs.

4. Conclusion

A series of new polymeric hole-transport materials was synthesized with partially oxygen-bridged, quasi-planar triphenylamine units either connected directly (P1), or coupled through m-benzene (P2), p-benzene (P3) or bithiophene (P4) π-spacers. These polymers demonstrated high amorphous stability comparable to PTAA.

Perovskite solar cell devices fabricated using P1 and P4 as additive-free HTMs gave high cell efficiencies, reaching 12.1% and 11.1% photoconversion, respectively, substantially higher than that of the reference additive-free PTAA-based device (4.8%).

The superior performance of P1 and P4 correlates with the higher hole mobility observed for these polymers compared to P2 and P3. The DFT calculations show that while the HOMOs of P1 and P4 have extended π-conjugation, the HOMOs of P2 and P3 are more localized.

These results demonstrate the importance of conjugated spacer units to provide additional delocalization in the HOMO. This is found to be a crucial aspect for the design of hole-transporting polymers based on quasi-planar triphenylamine scaffolds. New materials for perovskite solar cells based on this design principle will be reported in due course.

Acknowledgements

This work was partially supported by the ALCA (JPMJAL 1603), COI (JPMJCE 1307) programs of the Japanese Science and Technology Agency (JST), NEDO, Grant-in-Aid for JSPS Fellows (Grant Numbers 18F18342), Grant-in-Aid for Research Activity Start-up (19K23631), and Grant-in-Aid for Scientific Research (C) (19K05666). M.A.T. thanks the JSPS for Postdoctoral Fellowships for Research in Japan. We thank Prof. Kazunari Matsuda (Kyoto
University) for SEM measurements. 2D-GIXD experiments were performed at the BL19B2 and BL46XU of Spring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; Proposal No. 2017B1643, 2017B1834, 2019A1804). We thank Dr. Tomoyuki Koganezawa (JASRI) for advice on the 2D-GIXD measurements.

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