Novel Push-Pull Benzodithiophene-Containing Polymers as Hole-Transport Materials for Efficient Perovskite Solar Cells

Aleksandra N. Mikheeva 1,2, Ilya E. Kuznetsov 1, Marina M. Tepliakova 2, Aly Elakshar 2, Mikhail V. Gapanovich 1, Yuri G. Gladush 2, Evgenia O. Perepelitsina 1, Maxim E. Sideltsev 1, Azaliia F. Akhkiamova 1,3, Alexey A. Piryazev 1,3,4, Albert G. Nasibulin 2 and Alexander V. Akkuratov 1,*

1 Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry, Russian Academy of Sciences, FRC PCPMC RAS, Academician Semenov Avenue 1, 142432 Chernogolovka, Russia
2 Skolkovo Institute of Science and Technology, Nobel St. 3, 143026 Moscow, Russia
3 Department of Chemistry, Lomonosov Moscow State University, GSP-1, 1 Leninskiye Gory, 119991 Moscow, Russia
4 Sirius University of Science and Technology, 1 Olympic Ave., 354340 Sochi, Russia
* Correspondence: akkuratow@yandex.ru; Tel.: +7-4965227062

Abstract: Donor-acceptor conjugated polymers are considered advanced semiconductor materials for the development of thin-film electronics. One of the most attractive families of polymeric semiconductors in terms of photovoltaic applications are benzodithiophene-based polymers owing to their highly tunable electronic and physicochemical properties, and readily scalable production. In this work, we report the synthesis of three novel push–pull benzodithiophene-based polymers with different side chains and their investigation as hole transport materials (HTM) in perovskite solar cells (PSCs). It is shown that polymer P3 that contains triisopropylsilyl side groups exhibits better film-forming ability that, along with high hole mobilities, results in increased characteristics of PSCs. Encouraging a power conversion efficiency (PCE) of 17.4% was achieved for P3-based PSCs that outperformed the efficiency of devices based on P1, P2, and benchmark PTAA polymer. These findings feature the great potential of benzodithiophene-based conjugated polymers as dopant-free HTMs for the fabrication of efficient perovskite solar cells.

Keywords: benzodithiophene; conjugated polymers; hole-transport materials; perovskite solar cells; film-forming ability

1. Introduction

Perovskite solar cells (PSCs) are cost-effective and rapidly advancing photovoltaic technology showing great potential to compete with silicon solar cells, as well as to achieve strong positions on the market. Optimization of device structure and exploration of new absorber materials resulted in an unprecedentedly rapid increase in power conversion efficiency from ca. 4% to more than 25% [1,2]. Hole-transporting materials (HTMs) also play a crucial role in boosting performance and improving the operational stability of PSCs. In particular, individual or double-layered HTMs based on a combination of metal oxides and organic polymers can prevent the migration of the volatile byproducts of perovskite reversible decomposition from the device, so they could participate in the perovskite formation reaction enabling improved operation stability of PSCs [3,4]. Many various organic HTMs have recently been developed and investigated in PSCs. Among the most promising HTMs, the Spiro-OMeTAD (2,2′,7,7′-tetakis(N,N-di-p-methoxyphenyl-amine)9,9′-spirobifluorene) [5,6] and PTAA (poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine]) [7] are widely used. Unfortunately, these benchmark HTMs provide the impressive performance of PSCs only after doping, which usually suggests use of hygroscopic lithium salts coupled with further oxidation, thus leading to device stability mitigation [8]. In sum, the development of dopant-free, cost-effective HTMs with tunable electronic properties—high hole...
mobilities is of great importance. Moreover, good film formation properties of HTMs and uniform morphology of films are substantial aspects for the fabrication of high-performance PSCs [9,10]. In this regard, benzo[1,2-b:4,5-b']dithiophene-based (BDT) conjugated polymers can be considered as prospective HTMs. BDT is a fused tricyclic building block with a rigid planar structure and extended π-electron-delocalization, which facilitates efficient charge transport in BDT-based conjugated polymers [11]. Moreover, the BDT core can be easily functionalized by heteroaryl and alkyl groups in 4 and 8 positions, which also enables adjustment of the energy levels and morphology, which are important factors for improving the charge extraction and transport. Additionally, the coverage of perovskite with hydrophobic organic polymers enable the protection of the photoactive layer from moisture ingress.

Here, we report the synthesis of three novel BDT-based conjugated polymers and the investigation of these compounds, such as HTMs in PSCs. The polymers P1–P3 were designed according to the push–pull concept by combining BDT moieties bearing different alkyl side chains with benzothiadiazole acceptor and thiophene donor moieties to ensure favorable electronic and physicochemical characteristics, e.g., deep HOMO energy level, high charge mobilities, good solubility, and film formation properties (Figure 1).

Figure 1. Conjugated polymers P1–P3.

Variation of side chains on BDT core allowed additionally to investigate the effect of HTMs structure on their physico-chemical properties and charge-transport characteristics, which are important prerequisites for high performance of PSCs based on them.

2. Results and Discussion

The synthetic route for the preparation of benzodithiophene-based monomers D1–D3, benzothiadiazole-thiophene monomer M1 and conjugated polymers P1–P3 is shown in Figure 2. The reaction of benzo[1,2-b:4,5-b']dithiophene-4,8-dione (I) [12] with (4,5-dialkylthien-2-yl)lithium derivatives was followed by reduction of the corresponding diols with tin (II) chloride in hydrochloric acid afforded compounds 2–4. The monomers D1–D3 were obtained by lithiation of benzo[1,2-b:4,5-b']dithiophenes 2–4 with n-BuLi and quenching of lithium derivatives with trimethyltin chloride.

Monomer M1 was synthesized in three steps. First, 5,6-bis(octyloxy)-2,1,3-benzothiadiazole [13] (5) was brominated with bromine in acetic acid. Further palladium-catalyzed Stille coupling of compound 6 (1 eq., 1.82 mmol) and 2,5-bis(trimethylstannyl)thiophene (0.2 eq., 0.36 mmol) delivered monomer M1. Conjugated polymers P1–P3 were synthesized via Stille polycondensation reaction.
Figure 2. Synthesis of monomers D1–D3, M1 and conjugated polymers P1–P3. Conditions: i—(4,5-didecylthien-2-yl)lithium or (4-(2-ethylhexyl)-5-(methoxy)thien-2-yl)lithium or (5-(triisopropylsilyl)thien-2-yl)lithium, THF; ii—SnCl\(_2\)•2H\(_2\)O, 10% HCl; iii—BuLi, −78 °C, THF, TMEDA, SnMe\(_3\)Cl; iv—Br\(_2\), AcOH, 60 °C; v—2,5-bis(trimethylstannyl)thiophene, toluene, 110 °C, Pd(PPh\(_3\))\(_4\).

Polymers P1–P3 were precipitated with methanol, dried under reduced pressure, and then washed in Soxhlet apparatus with acetone, hexane, and chloroform. The chloroform fractions were concentrated on a rotary evaporator and an excess of methanol was added. The formed precipitates were collected by filtration, followed by drying in a nitrogen atmosphere (10−2 mm Hg). Relative molecular weight characteristics of conjugated polymers were determined by gel-permeation chromatography (GPC) against polystyrene standards (Figure S1). The obtained weight-average molecular weights of polymers P1–P3 are in the range of 13–22 kDa (Table 1). All polymers have good solubility in chloroform, toluene, and chlorobenzene at room temperature, which makes them suitable for deposition using solution-based techniques. The polymers were characterized by NMR spectroscopy (Figures S2–S4) and FTIR spectroscopy (Figure S5).
Molecules 2022, 27, 8333

4 of 13

Table 1. Physicochemical, optical, and electrochemical properties of polymers P1–P3.

|   | M<sub>w</sub>, kDa (M<sub>w</sub>/M<sub>n</sub>) | λ<sub>sol</sub><sup>max</sup> / λ<sub>film</sub><sup>max</sup> ABS | λ<sub>film</sub><sup>max</sup> PL / λ<sub>edge</sub><sup>ABS</sup> / nm | E<sub>opt</sub> / eV | E<sub>onset</sub> V vs. Fc/Fc<sup>+</sup> | HOMO, eV | LUMO*, eV | T<sub>d</sub>, °C |
|---|------------------|---------------------------|-----------------------------|----------------|-----------------|----------|---------|----------|
| P1 | 13.3 (2.3)       | 562/594,638/689          | 693                        | 1.84           | 0.40            | −5.20   | −3.36   | 322      |
| P2 | 14.7 (2.3)       | 572/587,632/683          | 678                        | 1.85           | 0.39            | −5.19   | −3.34   | 313      |
| P3 | 21.6 (1.8)       | 580,627/582,626/673      | 670                        | 1.86           | 0.36            | −5.16   | −3.30   | 329      |

* LUMO = HOMO + E<sub>opt</sub> – E<sub>gap</sub> (eV).

Thermal properties of polymers were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under an inert atmosphere. The 5% weight loss, which corresponds to the decomposition of materials, was observed at high temperatures from 313 °C to 329 °C for all materials (Figure 3d). Multistep destruction of macromolecules can probably be attributed to the scission of thermolabile octyloxy side chains followed by the destruction of the polymer backbone.

![Figure 3. Absorption spectra of polymers P1–P3 in 1,2-dichlorobenzene solution (a); absorption and emission spectra of thin films (b); cyclic voltammograms of polymer thin films (supporting electrolyte—0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile, scan rate—50 mVs<sup>−1</sup>, glassy carbon disc electrode) (c); TGA curves of polymers P1–P3 (d).](image-url)

No signals on the DSC curves were observed for polymers P2 and P3, which reveals the amorphous nature of materials in the solid state. Heating and cooling the DSC curves for polymer P1 showed low-intensity broad flat peaks with a T<sub>m</sub> of 158.8 °C and 189.7 °C, and T<sub>d</sub> of 163.9 °C (Figure S6). This implies certain self-organization of polymer P1 in the solid state, that might be attributed to the presence of four linear decyl side chains on thiophene fragments, which enhance non-covalent intermolecular interactions [14]. The XRD patterns of thin films of polymers P1–P3 revealed peaks at 2θ = 4–5°, which correspond to the short-range order, while the broad signal in the range of 2θ = 20–25° is typical for interactions via π–π stacking (Figure S7).
Optoelectronic properties of polymers were investigated by absorption spectroscopy, photoluminescence spectroscopy and cyclic voltammetry. All polymers exhibited two main absorption bands at 300–400 nm and 450–700 nm, which are attributed to \( \pi - \pi^* \) transitions and intramolecular charge transfer from donor to acceptor moieties, respectively (Figure 3).

In 1,2-dichlorobenzene solution, conjugated polymers demonstrated quite different optical properties, while in thin film spectra, \( \lambda_{\text{film}}^{\text{max}} \) and \( \lambda_{\text{film}}^{\text{edge}} \) are very similar. When comparing solution and film spectra (Figure S8), the most pronounced bathochromic shifts can be seen for absorption bands of P1 and P2 that may be due to strong self-aggregation of these polymers in the solid state. The minor red shift of the absorption band in the case of P3 suggests stronger aggregation of macromolecules even in solution at room temperature that was supported by temperature-dependent UV-visible spectra (Figure S8).

The emission bands in the photoluminescence spectra (PL) of polymers are shifted in a similar manner as in absorption spectra. The emission maxima for P1, P2, and P3 are located at 693 nm, 678 nm, and 670 nm, respectively. The Stokes shifts are in the range of 35.4–44.4 meV, which points to little structural difference between the excited and ground states of macromolecules. The lowest Stoke shift of 35.4 meV for P3 reveals insignificant reorganization energy of the charge carriers (polarons), which limits the intrinsic mobility of organic semiconductors [15,16]. Additionally, the most pronounced vibronic peak in the PL spectrum for P3 at 731 nm suggests a rigid character of macromolecules in the ground state. The optical bandgap of polymers was estimated as \( E_g = 1240/\lambda_{\text{int}} \), where \( \lambda_{\text{int}} \) is the wavelength at the intersection of corresponding absorption and emission bands. The \( E_g \) values of 1.84 eV, 1.85 eV, and 1.86 eV were found for P1, P2, and P3, respectively. The HOMO energy levels of the polymers were determined from the oxidation onsets (Figure 3c) as \( \text{HOMO} = -(E_{\text{ox}}^{\text{onset}} + 4.8) \) eV [17,18]. The onsets of oxidation potentials for P1, P2, and P3, were found to be 0.40 V, 0.39 V, and 0.36 V, corresponding to the HOMO energies of \(-5.20 \) eV, \(-5.19 \) eV, and \(-5.16 \) eV, respectively. Thus, the variation of side chains in the polymer backbone does not significantly affect the energy of frontier orbitals and energy bandgap (Table 1).

The matching of frontier orbital energies with a valence band (VB) and conductive band (CB) of perovskite is important for the selective extraction of one type of charge carriers (holes or electrons) and blocking of opposite charges in order to reduce the recombination processes. Since the HOMO and LUMO energies of polymers are well aligned with VB = \(-5.43 \) eV and CB = \(-3.93 \) eV of perovskite absorber (in this work, CH\(_3\)NH\(_3\)PbI\(_3\) or MAPbI\(_3\)), these compounds can be used as hole transport materials in perovskite solar cells [19].

The polymers P1–P3 were evaluated as HTM in PSCs with n-i-p architecture ITO/SnO\(_2/[6,6]\)-phenyl-C\(_{61}\)-butyric acid (PCBA)/MAPbI\(_3/P1–P3/MoO\(_3/Ag.\) Thin films of conjugated polymers P1–P3 were spin-coated from chlorobenzene solutions on top of the perovskite layer using preliminary optimized deposition conditions, and PTAA was used as a reference HTM. The detailed procedure was reported previously [20].

The photovoltaic characteristics of PSCs were investigated under AM 1.5 G (100 mW cm\(^{-2}\)) illumination. The highest PCE of 17.4% was obtained for PSCs with polymer P3 outperforming that with PTAA (PCE = 15.7%), P1 (PCE = 13.7%), and P2 (PCE = 12.4%), which is an encouraging result considering that HTM layer was processed without any kind of doping (Figure 4a, Table 2). Higher \( J_{SC} \) values of 20.9 mA cm\(^{-2}\) and FFs of 77% suggest that P3 possess sufficient charge transport properties. On the contrary, solar cells with polymers P1 and P2 exhibited lower fill factors, causing a remarkable decrease in efficiency. Additionally, forward and reverse scans of P2-based PSCs demonstrated noticeable hysteresis. This effect can result from inferior hole-transport properties or the hole-extraction ability of polymers P1 and P2 in contrast to P3, making it more suitable for HTM application [21].
Table 2. Hole mobilities of P1–P3 and photovoltaic performance of PSCs based on P1–P3.

| HTM  | \( \mu_{bh} \) cm\(^2\)V\(^{-1}\)s\(^{-1} \) | \( V_{OC}, \text{mV} \) | \( J_{SC}, \text{mA cm}^{-2} \) | FE, % | PCE, % |
|------|---------------------------------|----------------|----------------|------|--------|
| PTAA | n/a                             | 1020 \(^*\)  (1040 ± 14) \(^{**}\) | 20.9 (21.0 ± 0.9) | 74   | 15.7   |
| P1   | 3.63 \( \times \) 10\(^{-5} \)  | 1060 (1000 ± 51) | 19.9 (21.1 ± 0.9) | 65   | 13.7   |
| P2   | 2.89 \( \times \) 10\(^{-5} \)  | 1000 (980 ± 12)  | 20.7 (18.7 ± 1.3) | 60   | 12.4   |
| P3   | 4.10 \( \times \) 10\(^{-5} \)  | 1080 (1060 ± 11) | 20.9 (20.9 ± 0.5) | 77   | 17.4   |

\(^*\) maximal value (average ± standard deviation), \(^{**}\) average characteristics for sixteen devices.
Next, we estimated the hole mobilities of HTMs by a space-charge-limited current (SCLC) technique. Hole mobilities were found to be $3.63 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$, $2.89 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$, and $4.10 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$ for P1, P2, and P3, respectively. The higher hole mobility for P3 can be attributed to the better molecular packing due to improved interchain interactions arising from $\sigma(\text{Si})-\pi(\text{C})$ bond interactions that are in agreement with previously reported results [22,23]. Thus, enhanced characteristics of P3-based perovskite solar cells can be explained by higher hole mobilities of the HTM films.

In order to characterize the hole-extracting ability provided by the materials, we recorded steady-state photoluminescence (PL) spectra of samples of glass/perovskite/HTM and glass/perovskite as a reference (Figure 4b). Samples with P3 exhibited significant quenching of the PL intensity, which is usually attributed to the high hole extraction ability of the material. The signal observed at 660 nm corresponds to the intrinsic PL of P3. Surprisingly, the PL intensities of MAPbI$_3$/P1 and MAPbI$_3$/P2 bilayers were higher than that of bare perovskite film. Such an increase in the PL intensity may be the result of the passivation of trap states on the surface of perovskite and, therefore, mitigation of non-radiative recombination [24,25]. This conclusion is consistent with time-resolved PL measurements (Figure 4c). The effect is more pronounced in the case of P1 and P2 in accordance with steady-state PL. The exponential fitting of signal decay revealed the shortest charge carrier lifetime ($\tau_1 = 191.4$ ns) for the sample with P3, indicating a more efficient extraction of holes provided by this material [26,27].

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to explore the differences in the surface appearances of perovskite/P1–P3 samples (Figure S9). Both top-view SEM and AFM images revealed uniform and homogenous surface morphology, which means that the differences can not be found for freshly prepared devices on the microscale.

To evaluate the hydrophobicity and quality of coverage provided by polymers, we measured further the contact angle ($\theta$) of water on the surface of P1–P3 films deposited on perovskite (Figure 5). For all samples, $\theta = 96–99^\circ$ at the initial moment suggested the hydrophobic nature of the films. It can be seen that $\theta$ values for P3 film did not change with time, while for P1 and P2-based samples, the $\theta$ values rapidly decreased, indicating the interaction of water with the more hydrophilic perovskite layer. The measurements of contact angles on glass/polymer substrates showed similar results, with $\theta = 32–38^\circ$ for P1 and P2, and $\theta = 107^\circ$ for P3 (Figure S10). Optical microscopy examination of the substrates allowed us to note the circles, which appeared due to the reconstruction of the polymer layer after water deposition. In this case, the polymer film reconstruction facilitates contact between water and glass (Figure S11a). At the same time, neither defects nor similar circles form on the perovskite/P3 layer. To explore further polymer film reconstruction, the microphotographs of the samples glass/perovskite/P1–P3 just after water drop deposition were collected (Figure S11b). The spots on the surface of P1 and P2-based samples exposed to water are separated from undamaged perovskite by the rather thick boundary similar to the ones observed for perovskite-free samples. As for P3, there is a comparatively small area where perovskite is in contact with water and no similar boundaries appeared. Thus, we assume that the adhesion of polymer P3 to perovskite is strong enough to prevent its delamination and parting.

It is worth noting that in the devices, the layer deposited atop the polymer is inherently polar metal oxide (MoO$_3$). In the case of polymers P1 and P2, the layer deformation after MoO$_3$ deposition may occur, leading to defects on HTM/perovskite interface and, thus, to inferior performance of PSCs. Therefore, better adhesion of P3 films to perovskite probably enabled by a higher molecular weight of the polymer, resulting in the better quality of films and hence, improved performance of PSCs.

Thus, encouraging PCEs of 17.4% was achieved for devices with P3 as HTM without any doping. We envision that the double-layered polymer films such as P1/P3 or P2/P3 might be promising HTMs, due to their ability for passivation of perovskite defects along with good charge transport characteristics. The presented results provide good insights into
the role of molecular engineering on the physicochemical properties of novel BDT-based HTMs and their performance in perovskite solar cells.

![Image of contact angle changes](image-url)

**Figure 5.** Changes of contact angle of water on perovskite/HTM sample.

### 3. Materials and Methods

All solvents and starting compounds as benzo[1,2-b:4,5-b’]dithiophene-4,8-dione (CAS Number 32281-36-0), 2,5-bis(trimethylstannyli)thiophene (CAS Number: 86134-26-1), were purchased from Sigma-Aldrich (Saint Louis, MO, USA) or Acros Organics (Geel, Belgium) and used as received.

Molecular weight distribution was analyzed using gel-permeation chromatography (GPC) using Waters GPCV 2000 chromatograph (column PL-gel, 5 µm, MIXED-C, 300 × 7.5 mm) equipped with a refractometer. Tetrahydrofuran was used as an eluent. All measurements were carried out at 40 °C; the flow rate was 1 mL/min. “EMPOWER,” and Astra 5.3.2.20 software was used for data processing.

FT-IR spectra were recorded in the 400–4000 cm⁻¹ range (48 scans, resolution 4 cm⁻¹) using a Bruker ALPHA.

Absorption spectra for dilute solutions of polymers (1 × 10⁻⁴ M) and thin films deposited by spin-coating from 1 × 10⁻² M solutions on quartz substrates were measured in UV-visible region (300–800 nm) on scanning spectrophotometer SPECS SSP-705-1.

The ¹H and ¹³C NMR spectra were obtained using Bruker AVANCE 500 instrument. The AFM images were obtained using an NTEGRA PRIMA instrument (NT-MDT, Russia).

The cyclic voltammetry measurements were performed for thin films of the polymers P1–P3 deposited on a glassy carbon disc electrode by drop casting from chlorobenzene. The measurements were performed in a three-electrode electrochemical cell using a 0.1 M solution of Bu₄NBF₄ in acetonitrile as a supporting electrolyte, platinum wire as a counter electrode, and Ag/Ag⁺ (in 0.01 M acetonitrile) as a reference electrode. Ferrocene was used as an internal reference. The voltammograms were recorded using an ELINS P-20-X instrument at room temperature in the range −0.5–1.0 V with a potential sweep rate of 50 mV s⁻¹ [28].

The thermal properties of the polymers were investigated by thermal gravimetry analysis (TGA) using Q50 TA instruments under nitrogen with a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) was performed using a Netzsch DSC 214 Polyma instrument in the same conditions.

The J-V curves were recorded in the glovebox under the illumination (100 mW/cm²) provided by Newport Verasol AAA solar simulator using Advantest 6240A source-measurement units.

**Fabrication of solar cells with P1–P3 for the efficiency investigation**

The glass substrates covered with indium tin oxide (ITO, Kintec, 15 Ω/sq.) were preliminarily treated with ultrasonication in acetone, water, isopropanol and air-plasma (5 min). The 10% suspension of SnO₂ nanoparticles in water (Alfa Aesar, Kandel, Germany) was spin-coated at 4000 rpm in two steps for 20 sec. Further, samples were placed in
the cold heater and heated up to 165 °C for 10 min and annealed at this temperature
for 30 min. The passivation layer for SnO$_2$ (PCBA, 0.2 mg/mL in chlorobenzene (CB))
was spin-coated in the glovebox. The samples were annealed at 100 °C for 10 min. The
solution of MAPbI$_3$ perovskite (1.4M) was prepared by dissolving equimolar amounts
of methylammonium iodide and lead iodide in the mixture of dimethylformamide (80%)
and n-methylpyrrolidone (20%) to give a 1.4M solution of the perovskite ink. Perovskite
was spin-coated at 3000 rpm dynamically and left to dry for 20 min. In the next step,
samples were heated up to 80 °C for 10 min and annealed at this temperature for the next
5 min. Solutions of polymers (6 mg/mL in CB) were spin-coated at 2000 rpm, which was
preliminarily confirmed as the optimal deposition condition for each material. The layer
of MoO$_x$ (10 nm) was thermally evaporated on the full area (under $10^{-5}$ mbar). Finally,
the Ag top electrode (90–100 nm) was deposited using thermal evaporation through the
shadow mask, defining the area of the final cells to be 0.1 cm$^2$

**Synthesis of compounds**

Starting compounds 1a [29], 1b [30], 1c [31], 5 [32] were synthesized by previously
reported methods.

**Synthesis of compound 2**

Compound 2 was prepared using 2,3-didecylthiophene (1a) (5 g, 13.7 mmol), n-
BuLi 2.5 M in hexane (5.48 mL, 13.7 mmol), and benzo[1,2-b:4,5-b]dithiophene-4,8-dione
(1.58 g, 6.85 mmol). Then SnCl$_2$·2H$_2$O (6.2 g, 27.4 mmol) in 60 mL of 10% HCl was added
and the compound was isolated and purified as reported previously [29]. Yield: 80%

$^1$H NMR (CDCl$_3$, 500 MHz, $\delta$): 7.68 (d, 2H), 7.43 (d, 2H), 7.21 (s, 2H), 2.81 (t, 4H), 2.60 (t, 4H),
1.75–1.62 (m, 8H), 1.28 (m, 56H), 0.88 (m, 12H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$, $\delta$): 140.17, 138.86, 138.09, 136.36, 135.08, 129.84, 127.22, 124.14, 123.56, 31.91, 31.82, 30.79, 29.65, 29.63,
29.61, 29.55, 29.49, 29.43, 29.34, 28.31, 28.00, 22.67, 14.07.

**Synthesis of compound 3**

Compound 3 was prepared using 2-(2-ethylhexyl)-3-methoxythiophene (1b) (3.1 g,
13.7 mmol), n-BuLi 2.5 M in hexane (5.48 mL, 13.7 mmol), and benzo[1,2-b:4,5-b]dithiophene-
4,8-dione (1.58 g, 6.85 mmol). Then SnCl$_2$·2H$_2$O (6.2 g, 27.4 mmol) in 60 mL of 10% HCl
was added and the compound was isolated and purified as reported previously [30]. Yield:
64%

$^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 7.69 (d, 2H), 7.46 (d, 2H), 7.23 (s, 2H), 3.89 (s, 6H), 2.76 (d, 4H), 1.66 (m, 2H), 1.49–1.25 (m, 16H), 0.98–0.88 (m, 12H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$, $\delta$): 153.92, 139.09, 136.54, 134.13, 127.79, 124.39, 123.60, 123.01, 117.81, 59.34, 41.17, 32.79, 29.93, 29.11, 26.07, 23.28, 14.38, 11.11.

**Synthesis of compound 4**

Compound 4 was prepared using 1c (triisopropyl(thiophen-2-yl)silane) (3.3 g,
13.7 mmol), n-BuLi 2.5 M in hexane (5.48 mL, 13.7 mmol), and benzo[1,2-b:4,5-b]dithiophene-
4,8-dione (1.58 g, 6.85 mmol). Then SnCl$_2$·2H$_2$O (6.2 g, 27.4 mmol) in 60 mL of 10% HCl
was added and the compound was isolated and purified as reported previously [30]. Yield:
31%

$^1$H NMR (500 MHz, CDCl$_3$, $\delta$): 7.69 (d, 2H), 7.63 (d, 2H), 7.51 (d, 2H), 7.44 (d, 2H), 1.46 (m, 6H), 1.23 (d, 36H) ppm.

$^{13}$C NMR (126 MHz, CDCl$_3$, $\delta$): 145.29, 143.30, 142.39, 138.71, 137.76, 131.23, 128.83, 127.45, 123.52, 18.69, 11.89.

**Synthesis of compound D1**

Compound D1 was prepared using compound 2 (2.7 g, 3.1 mmol), 2.5 M n-BuLi
(3.1 mL, 7.8 mmol), TMEDA (1.86 mL, 12.4 mmol), and trimethyltin chloride (1.55 g,
7.8 mmol) according to previously reported methods [33]. Yield: 90% $^1$H NMR (500 MHz,
CDCl$_3$, $\delta$): 7.72 (s, 2H), 7.23 (s, 2H), 2.83 (t, 4H), 2.61 (t, 4H), 1.65–1.75 (m, 8H), 1.25–1.23 (m,
56H), 0.9–0.8 (m, 12H), 0.45–0.35 (m, 18H) ppm. $^{13}$C NMR (126 MHz, CDCl$_3$, $\delta$): 143.10,
141.91, 139.82, 138.00, 137.18, 135.77, 131.43, 129.83, 122.50, 31.94, 31.86, 30.86, 29.73, 29.70,
29.67, 29.55, 29.38, 28.35, 28.06, 22.71, 14.13, −8.34 ppm.

**Synthesis of compound D2**

Compound D2 was synthesized and purified following the method described for D1
using compound 3 (1.98 g, 3.1 mmol), 2.5 M n-BuLi (3.1 mL, 7.8 mmol), TMEDA (1.86 mL,
12.4 mmol), and trimethyltin chloride (1.55 g, 7.8 mmol) Yield: 68% $^1$H NMR (500 MHz,
Molecules 2022, 27, 8333

CDCl₃, δ): 7.73 (s, 2H), 7.25 (s, 2H), 3.92 (s, 6H), 2.78 (d, 4H), 1.68 (m, 2H), 1.50–1.25 (m, 16H), 1.00–0.88 (m, 12H), 0.45–0.40 (m, 18H) ppm. ¹³C NMR (126 MHz, CDCl₃, δ): 153.65, 143.17, 142.45, 137.19, 134.69, 131.17, 122.54, 122.50, 117.54, 59.19, 40.96, 32.62, 29.82, 28.95, 25.96, 23.11, 14.21, 10.98, −8.33 ppm.

Synthesis of compound D3

Compound D3 was synthesized and purified following the method described for D1 using compound 5 (2.07 g, 3.1 mmol), 2.5 M n-BuLi (3.1 mL, 7.8 mmol), TMEDA (1.86 mL, 12.4 mmol), and trimethyltin chloride (1.55 g, 7.8 mmol). Yield: 54%

¹¹H NMR (500 MHz, CDCl₃, δ): 7.77 (s, 2H), 7.67 (d, 2H), 7.43 (d, 2H), 1.45 (m, 6H), 1.22 (d, 36H), 0.42 (s, 18H) ppm.

¹³C NMR (126 MHz, CDCl₃, δ): 145.70, 143.06, 142.23, 137.26, 135.78, 135.09, 131.36, 128.64, 122.27, 18.69, 11.89, −8.41 ppm.

Synthesis of compound 6

Compound 6 was prepared using compound 5 (1 g, 2.55 mmol) and N-bromosuccinimide (0.703 g, 5.1 mmol) according to previously reported methods [34]. Yield: 92%

¹¹H NMR (CDCl₃, 600 MHz, δ): 4.20 (t, 4H), 1.94–1.91 (m, 4H), 1.57–1.55 (m, 4H), 1.42–1.34 (m, 16H), 0.93 (t, 6H) ppm.

Synthesis of compound M1

Compound M1 was prepared using 6 (1.0 g, 1.82 mmol), 2,5-bis(trimethylstannyl) thiophene (0.15 g, 0.36 mmol), toluene (50 mL) and tetrakis(triphenylphosphine)palladium(0) (10 mg, 0.47%mol) according to previously reported methods [33]. Yield: 24%

¹¹H NMR (CDCl₃, 500 MHz, δ): 8.51 (s, 2H), 4.20 (t, 4H), 4.12 (t, 4H), 1.92 (m, 4H), 1.55 (m, 4H), 1.43–1.21 (m, 40H), 0.88 (t, 6H), 0.81 (t, 6H) ppm.

Synthesis of polymers P1–P3

The polymers P1–P3 were synthesized using toluene as solvent, Pd₂dba₃ (4 mg, 1.5%mol) as the catalyst and (2-CH₃Ph)₃P (2 mg, 0.0066 mmol) as a ligand. When the polymers did not show further increase in molecular weight within 2–3 h, the reaction was stopped by adding of excess of 2-trimethyl(2-thienyl)stannane and after a 1 h excess of 2-bromothiophene. The general procedure of synthesis and purification has been reported previously [35].

Polymer P1

Polymer P1 was synthesized from M1 (0.30 g, 0.29 mmol) and D1 (0.364 g, 0.29 mmol) yield: 30%. Mₘ = 13.3 kDa, Mₘ/Мₙ = 2.3. ¹¹H NMR (CDCl₃, 500 MHz, δ): 9.27 (s); 8.65 (m); 7.45 (s); 4.20 (m, br); 2.88 (s); 2.67 (s); 2.04–2.02 (m, br); 1.48–1.24 (m, br); 0.89–0.82 (m, br) ppm. FT-IR (KBr, ν): 3430, 2931, 2851, 1631, 1569, 1462, 1426, 1373, 1284, 1221, 1177, 1079, 1026, 954, 892, 847, 812, 723, 527 cm⁻¹.

Polymer P2

Polymer P2 was synthesized from M1 (0.30 g, 0.29 mmol) and D2 (0.283 g, 0.29 mmol) yield: 40%. Mₘ = 14.7 kDa, Mₘ/Мₙ = 2.3. ¹¹H NMR (CDCl₃, 500 MHz, δ): 9.27 (s); 8.65 (m); 7.45 (s); 4.19 (m); 2.82 (s, br); 2.33 (m, br); 2.05–1.99 (m, br); 1.49–1.23 (m, br); 0.87–0.85 (m, br) ppm. FT-IR (KBr, ν): 3436, 2925, 2855, 1767, 1625, 1563, 1462, 1426, 1373, 1284, 1221, 1177, 1079, 1026, 954, 895, 847, 812, 723, 527 cm⁻¹.

Polymer P3

Polymer P3 was synthesized from M1 (0.30 g, 0.29 mmol) and D3 (0.291 g, 0.29 mmol) yield: 53%. Mₘ = 21.6 kDa, Mₘ/Мₙ = 1.8. ¹¹H NMR (CDCl₃, 500 MHz, δ): 9.63 (m, br); 8.39−8.16 (m, br); 7.72 (d, br); 7.49 (m, br); 4.30−4.16 (m, br); 2.33−1.98 (m, br); 1.57−1.24 (m, br); 0.95−0.85 (m, br) ppm. FT-IR (KBr, ν): 3441, 2925, 2854, 1643, 1563, 1465, 1429, 1376, 1278, 1206, 1171, 1082, 1028, 957, 895, 815, 726, 530 cm⁻¹.

4. Conclusions

In this work, we synthesized three novel benzodithiophene-based polymers with different side chains as hole transport materials for perovskite solar cells. It has been shown that polymer P3 containing trisopropylsilyl side groups exhibited better film formation properties and adhesion to perovskite absorber that, along with enhanced hole mobilities, resulted in the superior performance of devices. Encouraging PCE of 17.4% was achieved
for non-doped P3-based PSCs that outperformed the efficiency of devices based on P1 and P2 with alkyl or alkoxyl substituents and benchmark PTAA polymer. Furthermore, we put forward that double-layered polymer films such as P1/P3 or P2/P3 might be promising HTMs due to the good ability of P1 and P2 for passivation of perovskite defects along with the good charge transport characteristics of P3. These findings feature the great potential of benzodithiophene-based conjugated polymers as dopant-free HTMs for the fabrication of efficient perovskite solar cells.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27238333/s1, Figure S1: GPC chromatograms for polymers P1–P3 measured against polystyrene standards; Figures S2–S4: 1H NMR spectra of polymers; Figure S5: FT-IR spectra of polymers P1–P3; Figure S6: DSC curves for polymers P1–P3; Figure S7: XRD patterns of thin films of conjugated polymers P1–P3; Figure S8: Absorption spectra of polymers P1–P3 in 1,2-dichlorobenzene solution and thin films (a–c) and temperature-dependent UV-visible absorption spectra for P1–P3 in 1,2-dichlorobenzene solution (d–f); Figure S9: SEM (top) and AFM (bottom) images for perovskite/HTMs bilayer stacks: MAPbI3/P1 (a); MAPbI3/P2 (b); MAPbI3/P3 (c); Figure S10: Contact angle measurement of a water droplet placed on the surface of the polymer films; Figure S11: Optical images of glass substrates covered with polymers P1 (a), P2 (b), and P3 (c).

Author Contributions: Conceptualization, A.V.A. and M.M.T.; formal analysis, E.O.P.; M.V.G., A.A.P.; investigation, I.E.K., A.N.M., M.M.T., M.E.S., A.E., Y.G.G. and A.G.N.; writing-original draft preparation, A.V.A. and M.M.T.; writing-review and editing, A.V.A., M.M.T. and I.E.K.; supervision, A.V.A.; project administration, A.V.A. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Russian Foundation for Basic Research (project no. 20-03-00309) and the Ministry of Science and Higher Education of the Russian Federation within the project FFSG-2022-0004 (12211170041-8).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in this article.

Acknowledgments: This work was performed using the equipment of the Research Center FRC PCPMC RAS. We acknowledge the Advanced Imaging Core Facility (Skoltech) for the SEM measurements.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Min, H.; Lee, D.Y.; Kim, J.; Kim, G.; Lee, K.S.; Kim, J.; Paik, M.J.; Kim, Y.K.; Kim, K.S.; Kim, M.G.; et al. Perovskite Solar Cells with Atomically Coherent Interlayers on SnO2 Electrodes. Nature 2021, 598, 444–450. [CrossRef] [PubMed]
2. NREL. Best Research Efficiencies. Available online: https://www.nrel.gov/pv/Cell-Efficiency.html (accessed on 20 November 2022).
3. Liu, X.; Han, Q.; Liu, Y.; Xie, C.; Yang, C.; Niu, D.; Li, Y.; Wang, H.; Xia, L.; Yuan, Y.; et al. Light-Induced Degradation and Self-Healing inside CH3NH3PbI3-Based Solar Cells. Appl. Phys. Lett. 2020, 116, 253303. [CrossRef]
4. Tepliakova, M.M.; Mikheeva, A.N.; Somoy, P.A.; Statnik, E.S.; Korsunsky, A.M.; Stevenson, K.J. Combination of Metal Oxide and Polytriarylimine: A Design Principle to Improve the Stability of Perovskite Solar Cells. Energies 2021, 14, 5115. [CrossRef]
5. Liu, X.; Ding, X.; Ren, Y.; Yang, Y.; Ding, Y.; Liu, X.; Alsaedi, A.; Hayat, T.; Yao, J.; Dai, S. A Star-Shaped Carbazole-Based Hole-Transporting Material with Triphenylamine Side Arms for Perovskite Solar Cells. J. Mater. Chem. C 2018, 6, 12912–12918. [CrossRef]
6. Bakr, Z.H.; Wali, Q.; Fakharuddin, A.; Schmidt-Mende, L.; Brown, T.M.; Jose, R. Advances in Hole Transport Materials Engineering for Stable and Efficient Perovskite Solar Cells. Nano Energy 2017, 34, 271–305. [CrossRef]
7. Wang, Y.; Duan, L.; Zhang, M.; Hameiri, Z.; Liu, X.; Bai, Y.; Hao, X. PTAA as Efficient Hole Transport Materials in Perovskite Solar Cells: A Review. Solar RRL 2022, 6, 2200234. [CrossRef]
8. Luo, J.; Lin, F.; Xia, J.; Yang, H.; Zhang, R.; Malik, H.A.; Shu, H.; Wan, Z.; Han, K.; Wang, R.; et al. An Efficient and Hydrophobic Molecular Doping in Perovskite Solar Cells. Nano Energy 2021, 82, 105751. [CrossRef]
9. Cheng, F.; Cao, F.; Ru Fan, F.; Wu, B. Promotion Strategies of Hole Transport Materials by Electronic and Steric Controls for n–i–p Perovskite Solar Cells. ChemSusChem 2022, 15, e202200340. [CrossRef] [PubMed]
34. Kuznetsov, P.M.; Nikitenko, S.L.; Kuznetsov, I.E.; Proshin, P.I.; Revina, D.V.; Troshin, P.A.; Akkuratov, A.V. Thiazolothiazole-Based Conjugated Polymers for Blade-Coated Organic Solar Cells Processed from an Environment-Friendly Solvent. *Tetrahedron Lett.* 2020, 61, 152037. [CrossRef]

35. Luszczynska, B.; Akkuratov, A.V.; Szymanski, M.Z.; Susarova, D.K.; Dupont, B.G.R.; Babenko, S.D.; Inasaridze, L.N.; Bujak, P.; Troshin, P.A.; Ulanski, J. New Copolymers with Fluorinated and Non-Fluorinated Benzothiadiazole Units for Efficient Single Layer near Infra-Red Photodiodes with Fast Time Response. *Synth. Met.* 2018, 243, 67–74. [CrossRef]