An efficient lactone-to-lactam conversion for the synthesis of thiophene Pechmann lactam and the characterization of polymers thereof†

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Despite having unique structural features, e.g., high co-planarity and a strong polar bicyclic lactam structure, thiophene bipyrrrolylidene-2,2′(1H,1′H)-dione (TBPD) has been less explored as a dye, mainly due to the quite low yield in its synthesis via lactone-to-lactam conversion. We reported an efficient methodology for synthesizing TBPD in high yield using p-toluenesulfonic acid monohydrate and a catalytic amount of 4-dimethylaminopyridine in the chloroform solvent. From the newly synthesized series of TBPD-based donor–acceptor-type polymers, we fabricated organic field-effect transistors (OFETs), which were subjected to a systematic study on the relationship between film microstructure and charge transport. Among them, the annealed PTBPD-Th film revealed a more ordered lamellar packing with the highest number of interlayers and preferential edge-on orientation, yielding the best hole mobility (up to 0.46 cm² V⁻¹ s⁻¹). The improved synthesis of TBPD and our findings concerning related polymers could promote further research and development associated with the TBPD unit.

Introduction

The advantageous characteristics of dyes and pigments, such as good photosensitivity, brilliance, color, strength, transparency, and high thermal stability, make them suitable for use as coloring matter to hide the color tones of substrates due to the absorption and scattering of light.1–4 To date, many scientists have employed soluble organic dyes to synthesize complex semiconducting materials in the new flourishing field of organic electronics. In particular, bis-lactams containing dye motifs, e.g., diketopyrrolopyrrole (DPP),5–8 isoindigo (IIG),9–11 thiienoisindigo (TIIG),12–15 and thienobenzoisindigo (TBIG),16 have been extensively studied as accepting building blocks to develop top-performing donor–acceptor-type conjugated polymers for organic photovoltaics and organic field-effect transistors (OFETs).4 Their highly polar bis-lactam structure endows the related polymers with intriguing properties, including broad absorption, high mobility, and good ambient stability.16,18 A renaissance in the chemistry of dye molecules resulted from such extensive research and development activity, which inspired Zhang and co-workers to revitalize the old thiophene Pechmann dye (TPD) by converting it into a new soluble TPD lactam version, i.e., thiophene bipyrrrolylidene-2,2′(1H,1′H)-dione (TBPD) dye, and to report TBPD-based semiconducting materials.20–27 Similar to the aforementioned dyes, TBPD exhibits a planar and polar bis-lactam structure, yet a more red-shifted visible absorption (see Fig. 1).18,28 Alkyl side chains can be easily introduced as solubilizing groups into the pyrrole moiety in dyes, ensuring their solubility and thus the solution processability for purification and device fabrication. In contrast, the lactone (TPD)-to-lactam (TBPD) conversion reaction offers solution-processable TBPD bearing solubilizing chains but in very low yields (∼10%). Thus, despite its great potential for use in various optoelectronic devices, the insufficient yields in the synthesis of TBPD have limited its application scope as conjugated backbones in various semiconducting materials.

Through a comprehensive screening of reaction parameters, we reported an efficient lactone-to-lactam conversion for the synthesis of TBPD. The use of p-toluenesulfonic acid mono-

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†These authors contributed equally.
hydride with a catalytic amount of 4-dimethylamino pyridine (DMAP)\textsuperscript{29} can significantly improve the conversion yield of such a reaction. In addition, with sufficient TBPD monomer in hand, we prepared four new TBPD-based donor–acceptor-type polymers (PTBPD-Th, PTBPD-Th\textsubscript{2}, PTBPD-Se, and PTBPD-Se\textsubscript{2}) and explored the correlations between the structural modification of TBPD polymer backbones and charge transport properties. We hope that our results will contribute to further development of TBPD-based semiconductors, ultimately unveiling the full potential merits of the recently reported development of TBPD-based semiconductors, ultimately unveiling the full potential merits of the recently reported.

![Fig. 1](https://example.com/fig1.png)

Fig. 1 The structures of general lactam-based organic dyes and their UV-vis real spectrum. All of them were measured in the same concentration (2 mg mL\textsuperscript{-1} in CH\textsubscript{2}Cl\textsubscript{2} solution).

### Results and discussion

#### Synthesis and characterization

The amidation of lactone TPD, which was in turn prepared through Friedel–Crafts acylation with maleic anhydride and AlCl\textsubscript{3}, followed by intramolecular 5,5-exo-cyclization with CuCl and NH\textsubscript{4}Cl, was initially carried out according to previously reported procedures\textsuperscript{20} (2-octyldodecan-1-amine, CH\textsubscript{2}Cl\textsubscript{2}, 10% HCl, room temperature), affording the key TPD lactam analogues (TBPD, 1) in a low 7% yield (entry 1, Table 1). Therefore, other reaction conditions were investigated with the aim of improving the yield of the lactone-to-lactam conversion. First, to verify whether the system would be stabilized in highly polar solvents, N,N\textsuperscript{-}dimethylformamide (DMF)\textsuperscript{26,30} was used as the solvent in the reaction at evaluated temperatures, but no improvement in the yield was observed. It is worth mentioning that a color change from red to orange–yellow was observed at temperatures above 120 °C (entry 3, Table 1), which presumably stems from the thermal rearrangement of TPD from an exo-fused 5-membered type to an endo-fused 6-membered analog. During the screening of reaction conditions, we found that the yields were somewhat increased when slightly higher amounts of the alkyl amine and chloroform (CHCl\textsubscript{3}) solvent were employed (entries 5–7, Table 1). In addition, we also observed a slight improvement of the yield with the utilization of p-toluenesulfonic acid monohydrate (TsOH-H\textsubscript{2}O) instead of aqueous HCl. Furthermore, the TsOH-H\textsubscript{2}O/4-dimethylaminopyridine (DMAP, 5.0 mol%) system resulted in a significantly improved yield up to 40%, indicating that the presence of catalytic amounts of the nucleophilic base can efficiently promote the lactone-to-lactam conversion (entry 7, Table 1). This is attributable to the efficient intramolecular cyclization that leads to the formation of the exo-fused 5-membered bis-lactam in the presence of the catalytic auxiliary base. Table 1 summarizes the details of the reaction conditions examined in this study and relevant data.

Treatment of 3 with lithium diisopropylamide (LDA) at −78 °C, followed by the addition of 1,2-dibromo-tetrachloroethane, led to dibromide monomer 4 in 50% yield. Besides, various bistannylated heteroacene co-monomers (thiophene (Th), bithiophene (Th\textsubscript{2}), selenophene (Se), and biselenophene (Se\textsubscript{2})) were also synthesized according to previously published literature.\textsuperscript{6,15} With all the monomers in hand, a microwave-assisted Stille coupling polycondensation\textsuperscript{31,32} (Scheme 1) was carried out at 130 °C for 3 h in anhydrous chlorobenzene using P\textsubscript{d}(dba)\textsubscript{3} as a catalyst and P(o-toly1)\textsubscript{3} as the ligand, affording PTBPD-Th, PTBPD-Th\textsubscript{2}, PTBPD-Se, and PTBPD-Se\textsubscript{2}, respectively. The target polymers were purified by re-precipitation and Soxhlet extraction with methanol, acetone, and chloroform. The number-average molecular weights (M\textsubscript{n}) and the polydispersity index (PDI) of all polymers were measured by high temperature gel-permeation chromatography (GPC) using 1,2,4-trichlorobenzene as an eluent according to polystyrene standards. The M\textsubscript{n} values of PTBPD-Th, PTBPD-Th\textsubscript{2}, PTBPD-Se, and PTBPD-Se\textsubscript{2} were determined to be 34, 16, 29, and 33 kDa, with PDI values of 2.3, 2.6, 1.6, and 2.9, respectively. We observed a little variation in M\textsubscript{n} and PDI values of the

### Table 1 Amidation of lactone TPD

<table>
<thead>
<tr>
<th>Entry</th>
<th>Molar ratio of TPD to 2-octyldodecan-1-amine</th>
<th>Temperature</th>
<th>Solvent</th>
<th>Acid</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0 : 6.0</td>
<td>R.T.</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>10% HCl</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>1.0 : 6.0</td>
<td>70 °C</td>
<td>DMF</td>
<td>10% HCl</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>1.0 : 6.0</td>
<td>reflux</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>10% HCl</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>1.0 : 6.0</td>
<td>R.T.</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>10% HCl</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>1.0 : 6.0</td>
<td>R.T.</td>
<td>CHCl\textsubscript{3}</td>
<td>TsOH-H\textsubscript{2}O</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>1.0 : 6.6</td>
<td>R.T.</td>
<td>CHCl\textsubscript{3}</td>
<td>TsOH-H\textsubscript{2}O</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>1.0 : 6.6</td>
<td>R.T.</td>
<td>CHCl\textsubscript{3}</td>
<td>TsOH-H\textsubscript{2}O</td>
<td>40\textsuperscript{a}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Not determined because of the poor yield induced by structural rearrangement. \textsuperscript{b}Used 5.0 mol% of DMAP.
resulting polymers even under the same polymerization conditions. This is most likely explained by the different reactivity of the monomers. All the as-prepared polymers showed good solubility in common solvents such as chloroform, dichloromethane, toluene, THF, and chlorobenzene.

Thermogravimetric analysis (TGA) of all polymers showed their excellent thermal stability with high decomposition temperatures (see Fig. S16† and Table 2). On the other hand, from the differential scanning calorimetry (DSC) data shown in Fig. S17,† thermally induced transitions did not occur during the heating and cooling cycles of all the polymers.

Photophysical and electrochemical properties and computational studies

Fig. 2a and b show the UV-vis-NIR absorption of the TBPD-based polymers in chloroform solution and the as-spin-coated films. In all cases, two distinct absorption bands—a low-energy band [attributed to the intramolecular charge transfer (ICT)] and a high-energy band (arising from the $\pi-\pi^*$ transition)—covering the visible-to-near-infrared range of up to 1100 nm were observed.

The spectra of all the polymer films are characterized by slightly broader and red-shifted absorption features compared to those of the solution samples. Interestingly, a noticeable redshift in the solution and strong broadening in the solid state occur for PTBPD-Th and PTBPD-Se in comparison with the corresponding spectra of PTBPD-Th2 and PTBPD-Se2. These spectral observations imply that stronger intra- and/or inter-molecular interactions occur in PTBPD-Th and PTBPD-Se despite the extended $\pi$-conjugation length of the dimeric heteroacene units present in PTBPD-Th2 and PTBPD-Se2 (Th2 and Se2) compared to the corresponding single ones (Th and Se). Such absorption spectral characteristics were also observed in the thienoisoindigo-based polymers that we reported recently.15 The optical bandgaps ($E_{\text{opt}}^g$) from the absorption edge of the thin film were determined to be 1.13 eV for PTBPD-Th, 1.17 eV for PTBPD-Th2, 1.21 eV for PTBPD-Se, and 1.25 eV for PTBPD-Se2. The detailed photophysical properties of the polymers are listed in Table 2.

Electrochemical measurements using cyclic voltammetry (CV) were carried out to estimate the orbital energy levels (Fig. S9†). All the polymers show quasi-reversible oxidation and reduction waves in cathodic and anodic scans. The energies of the highest occupied molecular orbital (HOMO) and

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\lambda_{\text{sol max}}$ (nm)</th>
<th>$\lambda_{\text{film max}}$ (nm)</th>
<th>$E_{\text{opt}}^g$ (eV)</th>
<th>$E_{\text{HOMO}}^f$ (eV)</th>
<th>$E_{\text{LUMO}}^f$ (eV)</th>
<th>$E_{\text{HOMO}}^\text{calcd}$ (eV)</th>
<th>$E_{\text{LUMO}}^\text{calcd}$ (eV)</th>
<th>$T_d^{%}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTBPD-Th</td>
<td>839, 435</td>
<td>844, 439</td>
<td>1.13</td>
<td>−3.70</td>
<td>−5.10</td>
<td>1.40</td>
<td>−3.25</td>
<td>1.42</td>
</tr>
<tr>
<td>PTBPD-Th2</td>
<td>747, 445</td>
<td>805, 464</td>
<td>1.17</td>
<td>−3.63</td>
<td>−5.10</td>
<td>1.47</td>
<td>−3.22</td>
<td>−4.67</td>
</tr>
<tr>
<td>PTBPD-Se</td>
<td>863, 441</td>
<td>792, 471</td>
<td>1.21</td>
<td>−3.70</td>
<td>−5.05</td>
<td>1.35</td>
<td>−3.23</td>
<td>−4.61</td>
</tr>
<tr>
<td>PTBPD-Se2</td>
<td>759, 458</td>
<td>762, 450</td>
<td>1.25</td>
<td>−3.60</td>
<td>−5.05</td>
<td>1.45</td>
<td>−3.22</td>
<td>−4.58</td>
</tr>
</tbody>
</table>

$^a$ Chloroform solution. $^b$ Determined from the onset of the electronic absorption spectra. $^c$ Cyclic voltammetry determined with Fe/Fe + ($E_{\text{HOMO}}^\text{calcd}$ = −4.80 eV) as the external reference. $^d$ $E_{\text{opt}}^g$ = $E_{\text{LUMO}}^f$ − $E_{\text{HOMO}}^f$. $^e$ DFT calculation based molecular structures. $^f$ Decomposition temperature at 5% weight loss.
the lowest unoccupied molecular orbital (LUMO) were calculated from the onset of oxidation and reduction vs. ferrocene/ferrocenium (Fc/Fc\(^+\)). A summary of the results is given in Table 2 and Fig. S10\(^\ddagger\). The PTBPD-Se and PTBPD-Se\(^2\) polymers show slightly higher-lying HOMOs than PTBPD-Th and PTBPD-Th\(^2\), which suggests that the electron donating ability of the Se unit is somewhat stronger than that of Th. It is also interesting to note that relatively lower-lying LUMOs were observed on changing the backbone from dimer (Th\(^2\) and Se\(^2\)) to single heteroacene counterparts (Th and Se). The same variation trends of the frontier energy levels were found in B3LYP/6-31G density functional theory (DFT) calculations performed on the model compounds (Table 2). In addition, all theoretically optimized structures demonstrated very similar orbital distributions and high co-planarity (Fig. S11\(^\ddagger\)).

Thin film microstructure analyses

To investigate the thin film morphologies and molecular packing structures of the TBPD-based polymers, tapping-mode atomic force microscopy (AFM) and grazing incidence X-ray diffraction (GIXD) analyses were conducted. We prepared the polymer films by solution shearing of 1,2-dichlorobenzene (o-DCB) solutions on ~3 mg mL\(^{-1}\) of \(n\)-octadecyltrimethoxysilane (OTS)-treated SiO\(_2\)/Si substrates and subsequent annealing at the optimal temperature of 200 °C (see the OFET discussion below). All the annealed films showed very smooth nanoscale grains with a similar root-mean square roughness (\(R\text{_{RMS}}\)) of \(~0.7 \pm 0.1\) nm (Fig. S12\(^\ddagger\)). Among the four polymers, interestingly, PTBPD-Se\(^2\) exhibited a highly agglomerated surface morphology with a \(R\text{_{RMS}}\) of 0.868 nm and densely packed surface structures, which is indicative of the improved crystalline nanostructure of this polymer.

In addition to the intensified diffraction patterns after thermal annealing at 200 °C (Fig. 3 and S13\(^\ddagger\)), the GIXD data of all the annealed polymer films revealed multi-lamellar packing (\(n\text{00}\)) peaks along the out-of-plane direction. The measured crystallographic parameters of TBPD-based polymer films are provided in Table 3 (Table S1\(^\ddagger\) for the as-cast films). Notably, compared to other samples, PTBPD-Th displayed stronger and longer-range ordered lamellar peaks up to (400) with the highest coherence length \((L_c)\) of 222.6 Å. Additionally, PTBPD-Th showed the highest number of interlayers, i.e., combined effects of the layer distance and the crystallite size, \(L_c(100)/d(100)\), of 8.59 through the out-of-plane direction. These results suggest that PTBPD-Th has more ordered lamellar packing and stronger interchain interactions in the solid state with an enhanced crystalline size and lattice order, which

**Fig. 2** (a) UV-vis spectrum of TBPD-based polymers in chloroform solution and (b) the film state.

**Table 3** Crystallographic parameters of the annealed TBPD-based polymer film

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(q) (Å(^{-1}))</th>
<th>(d) (Å)</th>
<th>(L_c) (Å)</th>
<th>(L_c/d)</th>
<th>(q) (Å(^{-1}))</th>
<th>(d) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTBPD-Th</td>
<td>0.243</td>
<td>25.9</td>
<td>222.6</td>
<td>8.59</td>
<td>1.72</td>
<td>3.66</td>
</tr>
<tr>
<td>PTBPD-Th(^2)</td>
<td>0.280</td>
<td>22.4</td>
<td>186.5</td>
<td>8.32</td>
<td>1.76</td>
<td>3.57</td>
</tr>
<tr>
<td>PTBPD-Se</td>
<td>0.274</td>
<td>23.0</td>
<td>171.7</td>
<td>7.48</td>
<td>&quot;a&quot;</td>
<td>&quot;a&quot;</td>
</tr>
<tr>
<td>PTBPD-Se(^2)</td>
<td>0.286</td>
<td>22.0</td>
<td>170.2</td>
<td>7.74</td>
<td>1.74</td>
<td>3.61</td>
</tr>
</tbody>
</table>

\(a\) Not detected.
is generally believed to be beneficial and necessary for high-performance OFETs, since it leads to more efficient charge hopping characteristics. Compared to PTBPD-Th and PTBPD-Se, the polymers with extended electron donating groups (PTBPD-Th2 and PTBPD-Se2) exhibited decreased lamellar spacing, presumably due to the more interdigitated structure with the extended \( \pi \)-conjugated electron-donor moieties.\(^5\) It is also noteworthy that both Th-containing polymer films (PTBPD-Th and PTBPD-Th2) have significant edge-on orientation characteristics with the presence of a \( \pi \)-\( \pi \) stacking diffraction (010) peak along the in-plane direction, whereas this is hardly visualized in PTBPD-Se and PTBPD-Se2. Indeed, such a preferential edge-on configuration may result in good charge transport properties in OFETs.

**OFET performance**

Bottom-gate/top-contact OFETs were fabricated on OTS-treated SiO\(_2\)/Si substrates and measured under a N\(_2\) atmosphere to investigate the charge transport properties of the TBPD-based polymers. The device structure is provided in Fig. 4a. The polymer films were formed by solution shearing, which is a type of meniscus-guided coating method that affords enhanced crystallinity and uniformity of the processed films.\(^{33–35}\) The details of the device fabrication and measurement are provided in the Experimental section. All the fabricated OFET devices exhibited typical \( p \)-channel electrical characteristics (Fig. S14†). The devices were annealed at various temperatures to optimize their performance. Before annealing, the films exhibited relatively low electrical characteristics, as summarized in Table S2, but the hole mobilities of all the polymer films increased as the annealing temperature increased up to 200 °C. It should be noted that annealing at further elevated temperature induced a negative effect on the device performance. For example, the performance of the OFET based on the PTBPD-Se films was significantly degraded after the thermal treatment at 250 °C. Furthermore, we found that the use of a higher boiling point chlorinated solvent such as o-DCB remarkably improved the electrical performance in comparison with the CB-processed cases (see Table S3†). The representative transfer characteristics of the OFETs fabricated under the optimal conditions (o-DCB solution, 200 °C) are depicted in Fig. 4b, and the electrical performance parameters are summarized in Fig. 4c and Table 4. Among the TBPD-based polymers, the PTBPD-Th film prepared using the optimized conditions exhibited the highest \( \mu_h \) of up to 0.46 cm\(^2\) V\(^{-1}\) s\(^{-1}\) with a high on/off current ratio of \( 10^4 \)–\( 10^5 \), which is a comparable performance to that of the previously reported TBPD-based polymers.\(^{24,25,27}\)

The superior OFET performance of PTBPD-Th can be attributed to the improved morphological characteristics (e.g., large crystalline size, well-ordered lamellar packing, and preferential edge-on orientation), as discussed above. It should be noted that the PTBPD-Se2 film also exhibited a relatively good hole mobility most likely due to its dense lamellar structure, as can be inferred from the interlayer distance of \( \sim 21.9 \) Å, which is the shortest among the studied films.

Furthermore, to avoid mobility overestimation issues,\(^{36,37}\) which have recently attracted great attention in the characterization of the electrical performances of OFETs, we plotted the fitting lines for the observed maximum mobility, high gate bias region above the kink, and ideal behaviors, as shown in Fig. S15.† Based on the fitting lines, we calculated the mobilities of the high voltage region (\( \mu_{\text{high}} \)), the effective mobility (\( \mu_{\text{eff}} \)), and the reliability factors (\( R_{\text{sat}} \)) based on the reported method (Table S4†). The calibrated mobilities exhibited similar trends to the apparent maximum mobilities in the saturation regime, with a \( R_{\text{sat}} \) up to 63.4%.

These non-linear behaviors of the fabricated OFETs might have microscopic origins, including contact effects and non-equilibrium biasing of short-channels due to the narrow source–drain channel length of \( \sim 50 \) \( \mu \)m used in this work. Besides the short-channel effect, high local electric fields and current densities might lead to poorly controlled, nonlinear or unstable device characteristics. We believe that the use of a

**Table 4** Summary of electrical characteristics of the OFETs with TBPD-based polymer after annealing at 200 °C.

<table>
<thead>
<tr>
<th>Polymer( ^a )</th>
<th>( \mu_{\text{h,max}} ) ( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} )</th>
<th>( \mu_{\text{h,avg}} ) ( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} )</th>
<th>( \frac{I_{\text{on}}}{I_{\text{off}}} )</th>
<th>( V_{\text{th}} ) [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTBPD-Th</td>
<td>0.46</td>
<td>0.37 ( (\pm 0.066)^f )</td>
<td>( &gt;10^4 )</td>
<td>14.7</td>
</tr>
<tr>
<td>PTBPD-Th2</td>
<td>0.12</td>
<td>0.10 ( (\pm 0.012) )</td>
<td>( &gt;10^5 )</td>
<td>11.2</td>
</tr>
<tr>
<td>PTBPD-Se</td>
<td>0.11</td>
<td>0.066 ( (\pm 0.029) )</td>
<td>( &gt;10^5 )</td>
<td>25.5</td>
</tr>
<tr>
<td>PTBPD-Se2</td>
<td>0.28</td>
<td>0.22 ( (\pm 0.044) )</td>
<td>( &gt;10^5 )</td>
<td>17.5</td>
</tr>
</tbody>
</table>

\( ^a \)The FET performance of solution sheared polymer films fabricated with 3 mg mL\(^{-1}\) of 1,2-dichlorobenzene solution was measured under a nitrogen atmosphere (at least 15 devices). \(^f \)The maximum mobility of the FET devices \( (L = 50 \mu \text{m} \text{ and } W = 1000 \mu \text{m}) \). \(^f \)The average mobility of the FET devices \( (L = 50 \mu \text{m} \text{ and } W = 1000 \mu \text{m}) \). \(^f \)The on- and off-current ratio. \(^f \)The average threshold voltage. \(^f \)The standard deviation.
high source–drain voltage (−100 V) across short channels can cause enormous current densities and electric fields.

Conclusion

In summary, we have demonstrated that the lactone-to-lactam conversion can be efficiently catalyzed using TsOH·H₂O and a small amount of DMAP in CHCl₃ as the solvent, generating the TBPD motif with significantly improved yield. Besides, we have synthesized a series of donor-acceptor-type conjugated polymers (PTBPD-Th, PTBPD-Th₂, PTBPD-Se, and PTBPD-Se₂) consisting of TBPD and different heteroacenes (Th, Th₂, Se, and Se₂) to analyze and compare their optical, structural, morphological, and charge transport characteristics. Among the resulting polymers, the annealed PTBPD-Th shows the best hole mobility of 0.46 cm² V⁻¹ s⁻¹, which results from the advantageous changes in the morphology. This optimized methodology for the amidation of lactones, along with the comparative study herein presented, can not only contribute to further development of TBPD-based polymers for electronic applications, but also to gain deeper understanding of their structure–property relationships.

Experimental section

General analysis methods

The reagents and all starting materials were purchased from Aldrich Co., Alfa Aesar and TCI Co. and used without further purification. All solvents are ACS grade unless otherwise stated. Anhydrous THF was obtained by using a solvent purification system. ¹H NMR and ¹³C NMR of intermediates and monomers were conducted with 500 scans at 25 °C on a 400 MHz FT-NMR (Bruker) spectrophotometer using deuterated chloroform (CDCl₃) as a solvent and the ¹H NMR of polymers was recorded with 800 scans at 80 °C on a 600 MHz FT-NMR, VNMR 600 (Varian, USA) spectrophotometer using deuterated 1,2,2,2-tetrachloroethane (C₂D₂Cl₄) as a solvent. UV-vis-NIR spectra were collected on a Cary 5000 (Varian USA) spectrometer. DFT calculations were performed using the Gaussian 09 package with the nonlocal hybrid Becke three-parameter Lee–Yang–Parr (B3LYP) function and the 6-31G* basis set to obtain the HOMO and LUMO levels after optimizing the geometry of PTBPD-Th, Th₂, Se, and Se₂ using the same method. The number-average (Mₙ) and weight average (Mₗ) molecular weights, and the polydispersity index (PDI) of the polymer products were determined by gel permeation chromatography (GPC) with a Waters 150C GPC using a series of monodisperse polystyrenes as standards in 1,2,4-trichlorobenzene (HPLC grade) at 150 °C. Cyclic voltammetry (CV) measurements were performed on a Solartron electrochemical station (METEK, Versa STAT3) with a three-electrode cell in a 0.1 M tetra-n-butylammonium hexafluorophosphate (n-Bu₄NPF₆) solution in acetonitrile at a scan rate of 100 mV s⁻¹ at room temperature under argon. An Ag/Ag⁺ electrode, a platinum wire and a glass carbon disk were used as the reference electrode, counter electrode, and working electrode, respectively. The Ag/Ag⁺ reference electrode was calibrated using a ferrocene/ferrocenium redox couple as an external standard, whose oxidation potential is set at −4.8 eV with respect to zero vacuum level. The HOMO energy levels were obtained from the equation HOMO (eV) = −(E⁻₁(ox) − E⁻₁(ferrocene) + 4.8). The LUMO levels of polymers were obtained from the equation LUMO (eV) = −(E⁻₁(red) − E⁻₁(ferrocene) + 4.8). GIXD measurements were performed at the PLS-II 9A U-SAXS beamline of Pohang Accelerator Laboratory in Korea in accordance with previously reported literature.

Substrate preparation

A highly n-doped (100) Si wafer (<0.004 Ω cm) with a thermally grown SiO₂ (300 nm, Cᵢ = 11.5 nF cm⁻²) was utilized as the substrate and gate dielectrics. The SiO₂ surface was modified with n-octadecyltrimethoxysilane (OTS) as a self-assembled monolayer (SAM) according to the previously reported method. ³⁹ 3 mM of OTS solution in trichloroethylene was spin-coated on the piranha-treated wafer at 1500 rpm for 30 s. Then, the wafer was exposed to ammonia vapor for ~12 h to facilitate the formation of the SAM, followed by sonication in toluene, sequential washing, and drying. The water contact angle of the OTS treated surface was up to ~109°. The successful treatment of the highly hydrophobic OTS-modified surface is important for modifying the surface energy and polarity of the SiO₂ surface.

FET fabrication and measurement

FETs with bottom-gate/top-contact configuration were prepared to characterize the electrical performance of TBPD-based polymers. TBPD-based polymers were dissolved in anhydrous 1,2-dichlorobenzene (3 mg mL⁻¹) and the polymer films were solution sheared onto the substrate under a nitrogen atmosphere. 40 nm-thick Au layers were thermally evaporated onto the surface of polymer films to form source and drain electrodes with a channel length (L) of 50 μm and a width (W) of 1000 μm using a shadow mask. The electrical performance of the fabricated FETs was tested in a nitrogen-filled glovebox using a Keithley 4200 semiconductor parametric analyzer. Transfer characteristics (I₅S as a function of V₆G, where I₅S is the source–drain current and V₆G is the gate voltage) and output characteristics (I₅S as a function of V₅S at various V₆G, where V₅S is the drain voltage) were measured. The field-effect mobility was calculated in the saturation regime using the following equation:

\[ I₅S = \frac{W}{2L} \mu Cᵢ (V₆G - V₅T)² \]

The reliability factor of the saturation regime was calculated using the following equation:

\[ Rₛₐₜ = \left( \frac{\sqrt{I₅S} - I₅S₀}{|V₆G₀|} \right)^{0.2} \left( \frac{\partial \sqrt{I₅S}}{\partial V₆G₀} \right) \]

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The optimized amidation of lactone TPD

2-Decyl-tetradecylamine (1.77 g, 5.01 mmol) was added to a solution of compound 2 (250 mg, 0.76 mmol) in chloroform. After stirring for 10 min, DMAP (5.0 mol%, 4.64 mg) was added. The mixture was stirred overnight at ambient temperature. Then, p-toluenesulfonic acid monohydrate (1.01 g, 5.32 mmol) was added and stirred for 3 h. After that the reaction mixture was extracted with water and chloroform, and dried over MgSO4. The crude product was purified by column chromatography on silica gel using a 3:1 mixture of hexane/CH2Cl2 as an eluent to afford the product as a purple solid (304 mg, 40%). 1H NMR (CDCl3, 400 MHz): δ (ppm) = 7.46 (dd, J = 5.2, 1.2 Hz, 2H), 7.41 (dd, J = 4.1, 2 Hz, 2H), 7.12 (dd, J = 4.8, 3.6 Hz, 2H), 7.08 (s, 2H), 3.77 (d, J = 7.6 Hz, 4H), 1.64 (brs, 2H, 1.23–1.19 (m, 80H), 0.88–0.84 (m, 12H). 13C NMR (CDCl3, 100 MHz): δ (ppm) = 170.96, 145.21, 133.33, 128.24, 128.02, 127.89, 127.87, 103.53, 45.14, 37.42, 31.92, 31.90, 31.21, 29.91, 29.66, 29.64, 29.62, 29.54, 29.35, 29.33, 26.23, 22.67, 14.10. Different reaction conditions tested in this study for synthesizing TBPBD are summarized in Table 1.

Synthesis of 4

Compound 3 (1.0 eq.) was dissolved in anhydrous THF and cooled to −78 °C. After that LDA (3.0 eq., 1.8 M solution in THF) was added. The mixture was stirred overnight at ambient temperature. Then, 1,2-dibromotetrachloroethane (3.0 eq.) in THF was added to the reaction mixture at −78 °C, and after that the reaction mixture was added. The mixture was stirred overnight at ambient temperature. Then, Pd2(dba)3 (3.0 mol%) and P(o-tolyl)3 (12 mol%) were added to a solution of compound 25240 (1.0 eq.) was dissolved in anhydrous THF and cooled to −78 °C, and degassing for 10 min. After that, chlorobenzene was added after degassing for 10 min. After that PD[3][db]3 (3.0 mol%) and P(o-toly)l (12 mol%) were added to a microwave vial and the reaction mixture was further degassed and subsequently sealed. The vial was heated in a microwave reactor at 110 °C for 10 min and 130 °C for 3 h. After cooling to room temperature, it was poured into methanol and the resulting precipitate was filtered. The polymer was purified by Soxhlet extraction using methanol, acetone and hexane, and finally extracted with chloroform. The chloroform solution was then concentrated by evaporation and re-precipitated in methanol. The resulting deep purple colored solids were collected and dried overnight under vacuum.

PTPB-Th: Yield = 70%. 1H NMR (600 MHz, C2D2Cl4): δ (ppm) = 7.41–7.27 (br, 2H), 7.24–7.22 (br, 6H), 3.85 (br, 4H), 1.83 (br, 2H), 1.32 (br, 80H), 0.91 (br, 12H). Elemental Anal. Calcld for C68H106N2O2S3: C, 75.64; H, 9.90; N, 2.59; S, 8.91. Found: C, 73.81; H, 9.37; N, 2.27; S, 8.95. GPC: Mn = 34 kDa; Mw = 76 kDa; PDI = 2.26.

PTPB-Th2: Yield = 54%. 1H NMR (600 MHz, C2D2Cl4): δ (ppm) = 7.42 (br, 2H), 7.26–7.18 (br, 8H), 3.87 (br, 4H), 1.84 (br, 2H), 1.30 (br, 80H), 0.92 (br, 12H). Elemental Anal. Calcld for C72H108N2O2S2: C, 74.43; H, 9.37; N, 2.41; S, 11.04 Found: C, 73.72; H, 9.37; N, 2.27; S, 11.13. GPC: Mn = 16 kDa; Mw = 42 kDa; PDI = 2.60.

PTPB-Se: Yield = 60%. 1H NMR (600 MHz, C2D2Cl4): δ (ppm) = 7.41 (br, 3H), 7.31 (br, 1H), 7.23 (br, 4H), 3.86 (br, 4H), 1.84 (br, 2H), 1.30 (br, 80H), 0.93 (br, 12H). Elemental Anal. Calcld for C68H106N2O2S2Se: C, 72.49; H, 9.48; N, 2.49; S, 11.31. GPC: Mn = 29 kDa; Mw = 46.4 kDa; PDI = 1.60.

PTPB-Se2: Yield = 62%. 1H NMR (600 MHz, C2D2Cl4): δ (ppm) = 7.40–7.17 (br, 10H), 3.86 (br, 4H), 1.54 (br, 2H), 1.33 (br, 80H), 0.93 (br, 12H). Elemental Anal. Calcld for C72H108N2O2S4Se: C, 68.87; H, 8.67; N, 2.23; S, 5.54. Found: C, 66.54; H, 8.62; N, 1.80; S, 5.21. GPC: Mn = 11.4 kDa; Mw = 33 kDa; PDI = 2.89.

Conflicts of interest

There are no conflicts to declare.

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