SUPPORTING INFORMATION

Effects of Side-Chain Length and Shape on Polytellurophene Molecular Order and Blend Morphology

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Table 1. Calculated HOMO and LUMO energy levels and average inter-unit torsion angle for oligomers of P3HT, P3HS and P3HTe after optimization in the gas phase.

<table>
<thead>
<tr>
<th>polymer</th>
<th>heteroatom</th>
<th>HOMO Energy (eV)</th>
<th>LUMO Energy (eV)</th>
<th>inter-unit torsion angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3MT</td>
<td>S</td>
<td>-4.51</td>
<td>-1.91</td>
<td>20</td>
</tr>
<tr>
<td>P3MS</td>
<td>Se</td>
<td>-4.39</td>
<td>-2.11</td>
<td>0.16</td>
</tr>
<tr>
<td>P3MTe</td>
<td>Te</td>
<td>-4.64</td>
<td>-2.30</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Figure S1. Optimised structures viewed edge-on (a), and distribution of LUMO (b) and HOMO (c) molecular orbitals for oligomers of P3HT and P3HTe simulated using DFT. Side-chains have been reduced to methyl groups, orbital isosurfaces were drawn for a value of 0.02.

Figure S2. Evolution of the C=C and C-C modes of a hexamer of P3HTe with increasing inter-unit torsion angle, according to DFT simulations. Side-chains were reduced to methyl groups.
Figure S3. Normalised Raman spectra for bar-coated films of P3HT and P3HTe under 488 nm excitation; focusing on the low-intensity peaks between 450 and 1270 cm⁻¹. Labels indicate the peaks assigned to a heteroatom asymmetric stretch mode, spectra were normalised to the major C=C mode at 1390-1450 cm⁻¹ (not shown) and offset by 0.02 for clarity.

Figure S4. Normalised Raman spectra for neat P3HTe and a 2:1 blend of P3HTe:HDPE between 450 and 1900 cm⁻¹, with no new vibrational modes due to HDPE observed under 488 nm excitation. Both films were bar-coated at 140 °C.