Supporting Information

# Tellurophene-containing π-Conjugated Polymers with Unique Heteroatom-heteroatom Interactions by Post-elementstransformation of Organotitanium Polymer

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#### 1. Experimental Procedures

#### General Methods.

Nuclear magnetic resonance (NMR) spectra were measured on a JEOL ECP-300 instrument using tetramethylsilane as an internal standard (300 MHz, 75 MHz, and 94 MHz for <sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>125</sup>Te NMR respectively). Fourier transform infrared (FT-IR) spectra were measured on a Shimadzu IR Tracer-100 spectrometer (KBr disk). Gel permeation chromatography (GPC) measurements were performed on a Shimadzu LC-10AS liquid chromatograph equipped with Tosoh TSK-gel GMHHR-M tandem columns using tetrahydrofuran (THF) as an eluent at 35 °C. Polystyrene standards were used for calibration. UV-vis spectra were recorded on a Shimadzu UV-3100PC spectrometer in CHCl<sub>3</sub>. Electrochemical measurements were recorded on a VersaSTAT3 (Princeton Applied Research) potentiostat using a platinum (Pt) disk working electrode (d = 1.6 mm, BAS, Japan), a spiral Pt wire auxiliary electrode, and a silver (Ag) wire reference electrode under nitrogen stream. The single crystal X-ray analyses were carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer (Mo-Ka radiation,  $\lambda = 0.71075 \approx$ ). The data were collected at 93 K and the structure was solved by the direct methods (SIR2004) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The optimization and energy calculations were performed by the density functional theory (DFT) calculations, using the level of Beckethree-parameter-Lee-Yang-Parr hybrid (B3LYP) functional and the 6-31G\*\*/LANL2DZ with a split basis set (LANL2DZ for Te, and 6-31G\*\* for all other atoms) on the Gaussian16 program package.

#### Materials.

Titanium(IV) isopropoxide [Ti(OPr<sup>'</sup>)<sub>4</sub>], and ethynylbenzene (**M1H**) were obtained from Cica and were distilled under argon. Tellurium tetrachloride (TeCl<sub>4</sub>) and bromine (Br<sub>2</sub>) were obtained from Cica and used as received. Cyclopentyl methyl ether (CPME) was dried over sodium-benzophenone ketyl and distilled under nitrogen. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was dried over phosphorus pentoxide and distilled under nitrogen. 2-Ethynylanisole (**M1oOMe**),<sup>[1]</sup> 1-octyloxy-4-ethynylbenzene (**M1pOOc**),<sup>[2]</sup> and 1,4-diethynyl-2,5-bis(2-ethylhexyloxy)benzene (**1**)<sup>[3]</sup> were prepared by the previously reported methods. A diethyl ether solution of isopropylmagnesium chloride (Pr<sup>i</sup>MgCl) was prepared from 2-chloropropane and magnesium in diethyl ether. The polymerizations, the polymer reactions, and their corresponding model reactions were carried out under argon.

#### Synthesis of 2,5-Diphenyltellurophene (M3H).

To a 50 mL round-bottom flask containing ethynylbenzene (**M1H**, 0.20 g, 2.0 mmol), Ti(OPr<sup>'</sup>)<sub>4</sub> (0.40 g, 1.4 mmol), and CPME (20 mL), was added a diethyl ether solution of <sup>'</sup>PrMgCl (1.0 M, 2.8 mL, 2.8 mmol) under argon at -78 °C. After stirring for 30 min at that temperature, the mixture was warmed to -50 °C and stirred overnight. After the addition of TeCl<sub>4</sub> (0.40 g, 1.5 mmol) at -50 °C, the mixture was allowed to warm to ambient temperature and kept stirring for 3 h. The resulting mixture was poured into a sodium thiosulfate aqueous solution (10 mL). The organic layer was collected and the aqueous layer was extracted three times with diethyl ether (10 mL each). After drying over magnesium sulfate, the organic layer was evaporated under vacuum. Then, the residue was subjected to column chromatography on

SiO<sub>2</sub> with a mixed solvent of hexane and CH<sub>2</sub>Cl<sub>2</sub> (v/v = 2/1) as an eluent to give 2,5-diphenyltellurophene (**M3H**) in 88% yield (0.29 g, 0.88 mmol) as a white solid.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): 7.20-7.38 (aromatic, 6H), 7.48 (d, J = 6.9 Hz, aromatic, 4H), 7.83 (s, Te-C=C<u>H</u>, 2H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): 126.7, 127.6, 129.0, 133.9, 139.9, 148.3 ppm. <sup>125</sup>Te-NMR (CDCl<sub>3</sub>, 94 MHz): 748 ppm. IR (KBr disk): 3052, 3008, 1594, 1484, 1462, 1439, 1390, 1297, 1283, 1269, 1233, 1223, 1203, 1184, 1155, 1098, 1072, 1025, 995, 980, 962, 942, 903, 887, 809, 746, 685 cm<sup>-1</sup>. m.p. 224-225 °C (lit.<sup>[4]</sup> m.p. 224-225 °C). HRMS (DI): m/z calcd for C<sub>16</sub>H<sub>12</sub>Te (M<sup>+</sup>) 334.0001, found 339.9999.

## Synthesis of 2,5-Bis(2-methoxyphenyl)tellurophene (M3oOMe).

2,5-Bis(2-methoxyphenyl)tellurophene (**M3oOMe**) was likewise prepared by using **M1pOMe** (0.26 g, 2.0 mmol) as a starting material. The product (**M3oOMe**) was isolated in 86% yield (0.34 g, 0.86 mmol) as a pale yellow solid by column chromatography on SiO<sub>2</sub> with a mixed solvent of hexane and CH<sub>2</sub>Cl<sub>2</sub> (v/v = 2/1) as an eluent.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): 4.02 (s, -OC<u>H</u><sub>3</sub>, 6H), 6.92-7.01 (aromatic, 4H), 7.23 (ddd, J = 7.8 and 7.8 and 1.5 Hz, aromatic, 2H), 7.90 (dd, J = 7.8 and 1.5 Hz, aromatic, 2H), 8.30 (s, Te-C=C<u>H</u>, 2H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): 55.2, 111.4, 121.0, 124.4, 127.3, 128.6, 130.8, 138.4, 154.1 ppm. <sup>125</sup>Te-NMR (CDCl<sub>3</sub>, 94 MHz): 895 ppm. IR (KBr disk): 3009, 2967, 2932, 2831, 1589, 1575, 1490, 1478, 1458, 1431, 1324, 1309, 1293, 1284, 1267, 1244, 1174, 1118, 1084, 1046, 1023, 928, 815, 807, 743, 729 cm<sup>-1</sup>. m.p. 173-174 °C. HRMS (DI): m/z calcd for C<sub>18</sub>H<sub>16</sub>O<sub>2</sub>Te (M<sup>+</sup>) 394.0213, found 394.0211.

## Synthesis of 2,5-Bis(4-octyloxyphenyl)tellurophene (M3pOOc).

2,5-Bis(2-methoxyphenyl)-tellurophene (**M3pOOc**) was likewise prepared by using **M3pOOc** (0.46 g, 2.0 mmol) as a starting material. The product (**M3pOOc**) was isolated in 83% yield (0.49 g, 0.83 mmol) as a pale yellow solid by column chromatography on SiO<sub>2</sub> with a mixed solvent of hexane and CH<sub>2</sub>Cl<sub>2</sub> (v/v = 4/1) as an eluent.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): 0.89 (t, J = 6.6 Hz -C<u>H<sub>3</sub></u>, 6H), 1.19-1.85 (OCH<sub>2</sub>(C<u>H<sub>2</sub></u>)<sub>6</sub>CH<sub>3</sub>, 24H), 3.97 (t, J = 6.3 Hz, -OC<u>H<sub>2</sub></u>-, 4H), 6.86 (d, J = 8.7 Hz, aromatic, 2H), 7.39 (d, J = 8.7 Hz, aromatic, 4H), 7.65 (s, Te-C=C<u>H</u>, 2H), ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): 14.1, 22.6, 26.0, 29.2, 29.2, 29.3, 31.8, 68.2, 114.9, 127.8, 132.7, 132.7, 146.7, 159.0 ppm. <sup>125</sup>Te-NMR (CDCl<sub>3</sub>, 94 MHz): 730 ppm. IR (KBr disk): 2955, 2932, 2854, 1603, 1502, 1466, 1394, 1310, 1274, 1179, 1126, 1115, 1043, 1025, 999, 894, 832, 822, 799 cm<sup>-1</sup>.

#### Synthesis of $\pi$ -Conjugated Polymer Containing Tellurophene Units (3).

To a 50 mL round-bottom flask containing a CPME (20 mL) solution of **1** (0.19 g, 0.50 mmol) and Ti(OPr<sup>1</sup>)<sub>4</sub> (0.20 g, 0.70 mmol), was added a diethyl ether solution of <sup>1</sup>PrMgCl (1.0 M, 1.40 mL, 1.40 mmol) at -78 °C under argon. After stirring for 30 min at that temperature, the mixture was warmed to -50 °C and stirred overnight. After the addition of TeCl<sub>4</sub> (0.20 g, 0.75 mmol) at -50 °C, the resulting mixture was allowed to warm to ambient temperature and kept stirring for 3 h. Then, the resulting mixture was poured into a sodium thiosulfate aqueous solution (20 mL). The organic layer was collected and the aqueous layer was extracted three times with CH<sub>2</sub>Cl<sub>2</sub> (total 50 mL). After drying over magnesium sulfate, the organic layer was evaporated under vacuum. Then, the remaining solid was dissolved in a small amount of CH<sub>2</sub>Cl<sub>2</sub> (ca. 5 mL) and was precipitated into hexane (100 mL) to isolate **3** in 49% yield (0.12 g) as a red solid.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): 0.90 (br,-C<u>H</u><sub>3</sub>, 12H), 1.08-1.92 (OCH<sub>2</sub>C<u>H</u>(C<u>H</u><sub>2</sub>CH<sub>3</sub>)C<u>H</u><sub>2</sub>C<u>H</u><sub>2</sub>C<u>H</u><sub>2</sub>CH<sub>3</sub>, 18H), 4.12 (br, -OC<u>H</u><sub>2</sub>-, 4H), 7.47 (br, aromatic, 2H), 8.25 (br, Te-C=C<u>H</u>, 2H) ppm; IR (KBr disk): 2957, 2928, 2873, 1599, 1497, 1466, 1457, 1406, 1380, 1291, 1283, 1205, 1031,1013 796 cm<sup>-1</sup>.

# Synthesis of 2,5-Bis(2-methoxyphenyl)-1,1-dibromotellurophene (M4oOMe).

To a solution of **M3oOMe** (0.20 g, 0.50 mmol) in  $CH_2CI_2$  (2.5 mL) was added  $Br_2$  (0.048 g, 0.60 mmol) at ambient temperature. After 5 min, the reaction mixture was evaporated to dryness under reduced pressure and the residue was recrystallized from  $CH_2CI_2$  and hexane to give 2,5-bis(2-methoxyphenyl)-1,1-dibromotellurophene (**M4oOMe**) in 90% yield (0.25 g, 0.45 mmol) as red crystals.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): 4.07 (s,  $-OCH_3$ , 6H), 7.02-7.15 (aromatic, 4H), 7.37 (ddd, J = 7.5 Hz and 7.5 and 1.5 Hz, aromatic, 2H), 7.70 (s, Te-C=CH, 2H), 7.72 (dd, J = 7.5 and 1.5 Hz, aromatic, 2H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): 56.2, 112.0, 122.0, 122.4, 126.0, 130.9, 135.7, 149.8, 154.0 ppm. <sup>125</sup>Te-NMR (CDCl<sub>3</sub>, 94 MHz): 914 ppm. IR (KBr disk): 3001, 2849, 1588, 1473, 1458, 1431, 1328, 1312, 1285, 1263, 1240, 1179, 1113, 1064, 1032, 925, 810, 807, 721, 7 688 cm<sup>-1</sup>. HRMS (DI): m/z calcd for C<sub>18</sub>H<sub>16</sub>O<sub>2</sub>Te (M<sup>+</sup>) 394.0213, found 394.0211.

# Synthesis of 2,5-Bis(4-octyloxyphenyl)-1,1-dibromotellurophene (M4pOOc).

Similar to the case of **M4oOMe** was prepared from **M3pOOc** (0.29 g, 0.50 mmol). Purification of **M4pOOc** was carried out by recrystallization from  $CH_2Cl_2$  and hexane to give 2,5-Bis(4-ethylhexyloxyphenyl)-1,1-dibromotellurophene (**M4pOOc**) in 93% yield (0.35 g, 0.47 mmol) as red crystals.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): 0.89 (t, J = 7.2 Hz -CH<sub>3</sub>, 6H), 1.19-1.85 (OCH<sub>2</sub>(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>, 24H), 4.01 (t, J = 6.3 Hz, -OCH<sub>2</sub>-, 4H), 6.96 (d, J = 8.4 Hz, aromatic, 2H), 7.23 (s, Te-C=CH, 2H), 7.52 (d, J = 8.4 Hz, aromatic, 4H) ppm. <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz): 14.1, 22.6, 26.0, 29.1, 29.2, 29.3, 31.8, 68.3, 115.6, 125.4, 128.9, 136.4, 161.1, 161.8 ppm. <sup>125</sup>Te-NMR (CDCl<sub>3</sub>, 94 MHz): 730 ppm. IR (KBr disk): 2956, 2906, 2856, 1600, 1503, 1465, 1376, 1275, 1260, 1178, 1098, 1023 cm<sup>-1</sup>.

# Synthesis of $\pi$ -Conjugated Polymer Containing 1,1-Dibromotellurophene Units (4).

To a solution of **3** (0.10 g, 0.20 mmol unit) in  $CH_2Cl_2$  (1.0 mL) was added  $Br_2$  (0.040 g, 0.25 mmol) at ambient temperature. After 5 min, the reaction mixture was precipitated into hexane (50 mL) to isolated **4** in 88% yield (0.12 g, 0.18 mmol unit) as a purple solid.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz): 0.90 (br, -C<u>H</u><sub>3</sub>, 12H), 1.08-1.92 (OCH<sub>2</sub>C<u>H</u>(C<u>H</u><sub>2</sub>CH<sub>3</sub>)C<u>H</u><sub>2</sub>C<u>H</u><sub>2</sub>C<u>H</u><sub>2</sub>CH<sub>3</sub>, 18H), 3.62-4.28 (-OC<u>H</u><sub>2</sub>-, 4H), 6.57-7.84 (aromatic and Te-C=C<u>H</u>, 4H) ppm; IR (KBr disk): 2960, 2924, 2876, 1601, 1489, 1470, 1452, 1412, 1383, 1288, 1202, 1291, 1283, 1202, 1030, 1011, 784 cm<sup>-1</sup>.

## 2. NMR Spectra



Figure S1. <sup>1</sup>H-NMR spectrum of **M3H**.



Figure S2. <sup>13</sup>C-NMR spectrum of **M3H**.



Figure S3. <sup>125</sup>Te-NMR spectrum of **M3H**.



Figure S4. <sup>1</sup>H-NMR spectrum of **M3oOMe**.



Figure S5. <sup>13</sup>C-NMR spectrum of **M3oOMe**.















Figure S9. <sup>125</sup>Te-NMR spectrum of **M3pOOc**.



Figure S10. <sup>1</sup>H-NMR spectrum of **M4oOMe**.



Figure S11. <sup>13</sup>C-NMR spectrum of **M4oOMe**.



Figure S12. <sup>125</sup>Te-NMR spectrum of **M4oOMe**.



Figure S13. <sup>1</sup>H-NMR spectrum of **M4pOOc**.



Figure S14. <sup>13</sup>C-NMR spectrum of **M4pOOc**.







Figure S16. <sup>1</sup>H-NMR spectrum of **3**.



Figure S17. <sup>1</sup>H-NMR spectrum of **4**.

# 3. Density Functional Theory (DFT) Calculations



Figure S18. Optimized structures for **M3H** (a), **M4H** (b), **M3oOMe** (c), and **M4oOMe** (d) with a split basis set (LANL2DZ for Te and 6-31G\*\* for all other atoms).



Figure S19. HOMO, LUMO energy levels, and their frontier molecular orbitals of **M3oOMe** and **M4oOMe** in their optimized ground states with a split basis set (LANL2DZ for Te and 6-31G\*\* for all other atoms).



Figure S20. Cyclic voltammograms of **M3oOMe** (a), **3** (b), **M4oOMe** (c), and **4** (d) (conditions: 0.10 M tetra-*n*-butylammonium hexafluorophosphate, at a sweep rate of 100 mVs<sup>-1</sup>, **M3oOMe** and **M4oOMe**: in acetonitrile solutions and **3** and **4**: in film on a Pt disk immersed in acetonitrile).

## 5. Crystal Structures

Identiification code	M3oOMe	M4oOMe
Empirical formula	C <sub>18</sub> H <sub>16</sub> O <sub>2</sub> Te	C <sub>18</sub> H <sub>16</sub> Br <sub>2</sub> O <sub>2</sub> Te
Formula weight	391.92	551.73
Temperature	-180.0 °C	-180.0 °C
Wavelength	0.71075 Å	0.71075 Å
Crystal system	orthorhombic	triclinic
Space group	Pca2₁	P-1
Unit cell dimension	a = 18.407(2) Å	a = 9.6046(9) Å α = 99.405(3)°
	b = 13.221(2) Å	$b = 10.539(1) \text{ Å } \beta = 103.196(3)^{\circ}$
	c = 6.2891(6) Å	$c = 19.635(2) \text{ Å } v = 102.209(4)^{\circ}$
Volume	1530 5(3) Å <sup>3</sup>	1843 9(4) Å <sup>3</sup>
7	4	4
– Density (calculated)	1.701 g/cm <sup>3</sup>	1.987 a/cm <sup>3</sup>
Absorption coefficient	19.451 cm <sup>-1</sup>	59.664 cm <sup>-1</sup>
F(000)	768.00	1048.00
Crvstal size	0.50 x 0.10 x 0.01 mm	0.780 x 0.100 x 0.100 mm
Reflections collected	7986	17317
Independent reflections	2818 (R <sub>int</sub> = 0.0724)	8136 (Rint = 0.0879)
Absorption correction	empirical	empirical
Max. and min. transmission	0.026 and 0.551	0.026 and 0.551
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Goodness-of-fit on F <sup>2</sup>	1.020	1.887
Final R indices [I>2sigma(I)]	0.0472	0.1255
R indices (all data)	R1 = 0.0640, wR2 = 0.1507	R1 = 0.1621, wR2 = 0.3573
Largest diff. peak and hole	1.58 and -1.63 e <sup>-</sup> /Å <sup>3</sup>	3.48 and -2.59 e <sup>-</sup> /Å <sup>3</sup>

Table S1. Crystal data and structure refinement for M3oOMe and M4oOMe



Figure S21. ORTEP drawing of M4oOMe showing two independent molecules in the asymmetric unit.

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