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Polymerization of Tellurophene Derivatives by Microwave-Assisted Palladium-Catalyzed *ipso*-Arylative Polymerization**

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Abstract: *We report the synthesis of a tellurophene-containing low-bandgap polymer, PDPPTe2T, by microwave-assisted palladium-catalyzed ipso-arylative polymerization of 2,5-bis[(α-hydroxy-α,α-diphenyl)methyl]tellurophene with a diketopyrrolopyrrole (DPP) monomer. Compared with the corresponding thiophene analog, PDPPTe2T absorbs light of longer wavelengths and has a smaller bandgap. Bulk heterojunction solar cells prepared from PDPPTe2T and $PC_{71}BM$ show PCE values of up to 4.4 %. External quantum efficiency measurements show that PDPPTe2T produces photocurrent at wavelengths up to 1 μm. DFT calculations suggest that the atomic substitution from sulfur to tellurium increases electronic coupling to decrease the length of the carbon–carbon bonds between the tellurophene and thiophene rings, which results in the red-shift in absorption upon substitution of tellurium for sulfur.*

Forming carbon–carbon bonds is fundamental to the construction of organic compounds. In the synthesis of π-conjugated organic polymer containing polyaryl and/or polyheteroaryl structures, the most common synthetic strategies use transition metal-mediated reactions to form carbon–carbon bonds between the aryl rings. For example, poly(3-alkylthiophene)s, the most-studied polymers in organic photovoltaic (OPV) devices, have been prepared by a range of transition metal-mediated aryl coupling methodologies including McCullough,[1] Rieke,[2] and Grignard metathesis (GRIM)[3] methods as well as Stille[4] and Suzuki[5] cross-coupling reactions. Properties critical to polymer performance such as molecular weight, polydispersity, and regioregularity are controlled by the efficiency and regioregularity of the specific coupling reactions used for polymerization.[6] Typically, these reactions involve the coupling of aryl halide with an organometallic aryl reagent. The formation of aryl–aryl bonds through the cleavage of aryl–carbon bonds would allow polymerization to proceed without the need for reactive inorganic leaving groups, however, there are a limited number of examples of such reactions because of the high bond dissociation energy for carbon–carbon bonds.[7] We have previously found that the use of *ipso*-arylative cross-coupling reactions offers advantages in the coupling reactions of tellurophene derivatives—specifically diphenylcarbinol-substituted benzotellurophenes—and these results have prompted us to further investigate this methodology for the challenge of preparing tellurophene-based conjugated polymers.[8]

The recent synthesis of solution-processable poly(3-alkyltellurophene)s by GRIM polymerization[9] has proven the great potential of tellurophene-based materials for optoelectronic applications. In comparison with poly(3-alkylthiophene)s, Seferos and co-workers have observed red-shifted absorption spectra and smaller bandgaps from poly(3-alkyltellurophene)s.[9] In a related development, Choi and co-workers have prepared a tellurophene-containing low-bandgap polymer by Stille cross-coupling and reported that replacing sulfur atoms with tellurium atoms in conjugated polymers reduces the bandgap and improves the hole mobility,[10] potentially enhancing the performance of OPV materials.

Tellurophene, the Group 16 tellurium analog of thiophene and selenophene, is an interesting building block for organic optoelectronic materials because tellurium is a metalloid and its large spin–orbit coupling may allow tellurophene-based semiconductors to populate long-lived triplet excited states[11] by intersystem crossing. The longer triplet exciton lifetimes should increase exciton diffusion lengths allowing more photocurrent collection and result in higher solar cell power conversion efficiencies (PCEs).[12] However, the paucity of synthetic methods available for tellurophene synthesis and modification has hampered the more detailed investigation of devices based on tellurophene derivatives. Herein, we describe the first example of palladium-catalyzed *ipso*-arylative copolymerization of a tellurophene monomer (**1**) with a diketopyrrolopyrrole (DPP) unit (**2**) (Scheme 1), in a method complementary to widely used Stille[10] and Suzuki–Miyaura polymerizations, and demonstrate use of the resulting polymer in photovoltaic devices. We compare the optoelectronic properties of the tellurophene-based polymer with those of its thiophene analogue and illustrate

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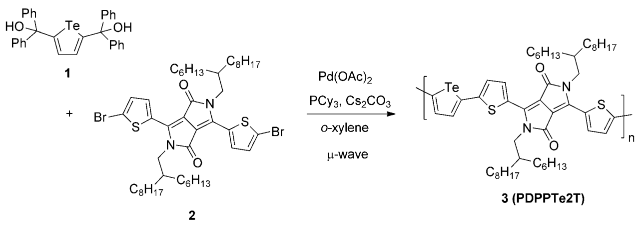
Supporting information for this article (general experimental details, synthesis and characterization for compounds, UV/Vis absorption spectra, cyclic voltammetry, gel-permeation chromatography, details of device fabrications, computation details, and NMR spectra) is available on the WWW under http://dx.doi.org/10.1002/anie.201406068.



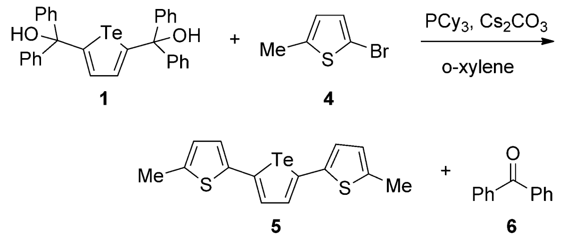
Scheme 1. Palladium-catalyzed *ipso*-arylative polymerization.

potential applications of tellurophene-containing materials in OPVs.

We designed a new monomer, 2,5-bis[(α-hydroxy-α,α-diphenyl)methyl]tellurophene (**1**), for copolymerization with dihaloarenes based on our recent synthesis of a molecular semiconductor through the palladium-catalyzed *ipso*-arylative coupling of a benzotellurophenyl-substituted diphenylcarbinol with the DPP core **2**.[8] In this approach, the organic benzophenone leaving group enables coupling reactions to be run without generation of a stoichiometric amount of trialkyltin halides, which are toxic and can remain as potential impurities for OPV devices,[13] or the synthesis of boronic acid-functionalized monomers with their accompanying difficulties in purification.[14] Tellurophene monomer **1** can be easily prepared on multi-gram scales by addition of dilithiated tellurophene to benzophenone and purified by flash chromatography (isolated yields of 65%, Supporting Information (SI)). Monomer **1** has been stored for more than a year under refrigeration without any observable degradation.

Model coupling reactions with tellurophene monomer **1** (1 equiv) and 2-bromo-5-methylthiophene **4** (3 equiv) as substrates were carried out with $Pd(OAc)_2$ as the catalyst precursor, PCy_3 as a ligand, and Cs_2CO_3 as a base in *o*-xylene under conventional heating at 140 °C and under microwave irradiation[15] at 180 °C (Table 1). After careful inspection of the reaction mixtures, only product **5** (isolated yields of 93% for conventional heating and 78% for microwave irradiation, respectively) and benzophenone **6** could be observed, suggesting that monomer **1** exclusively undergoes *ipso*-arylation, as has previously been observed in *ipso*-arylative couplings with 2-thienyl- and 2-furyl(diphenyl)methanol,[16,17] in preference to the undesired *ortho*-arylation pathway that can occur with carbinol leaving groups.

Table 1: Model coupling reactions.



Entry	Reagents (equiv)	Conditions	Yield [%][c]
1	$Pd(OAc)_2$ (0.05), PCy_3 (0.10), Cs_2CO_3 (4.0)	140 °C[a]	93
2	$Pd(OAc)_2$ (0.05), PCy_3 (0.30), Cs_2CO_3 (6.0)	180 °C[b]	78

[a] By conventional heating for 72 h. [b] By microwave irradiation for 1 h. [c] Yield of isolated product.

The high yields and regioselectivities observed with the model substrate led us to investigate the polymerization of tellurophene monomer **1** with the DPP-based monomer 3,6-bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-di(2-hexyldecyl)-pyrrolo[3,4-*c*]pyrrolo-1,4-dione (**2**, Scheme 1) at 180 °C for 3 h under microwave irradiation, to enable rapid polymerization[18] and facilitate the formation of high molecular weight polymer.[19] In aliquots withdrawn from the polymerization mixture for spectroscopic analysis (SI), both the absorption peaks and absorbance onset were observed to shift toward the red as the polymer chains grew, with the onset of absorption reaching almost 1000 nm after 2 h.

During purification by Soxhlet extraction, PDPPTe2T (**3**) was separated into a lower-molecular weight chloroform-soluble fraction (SEC vs polystyrene standards: $M_n = 8.0\ \mathrm{kg\,mol^{-1}}$; $Đ = 3.8$) and a higher-molecular weight chloroform-insoluble fraction (SEC vs polystyrene standards: $M_n = 23.2\ \mathrm{kg\,mol^{-1}}$; $Đ = 3.7$). The high molecular weight fraction was observed to be soluble in chloroform ($\approx 7.5\ \mathrm{mg\,mL^{-1}}$) at 80 °C.

Regardless of molecular weight, PDPPTe2T exhibited a red-shifted absorption relative to PDPP3T,[20] with two local maxima near 900 nm and 810 nm in *o*-dichlorobenzene (ODCB) (Figure 1 a). As observed in PDPP3T absorption spectra,[20] the intensity of the longer wavelength peak becomes more pronounced as polymer molecular weight increases (Figure 1 a). From the onset of absorption, we estimated the optical bandgap of PDPPTe2T ($M_n = 23.2\ \mathrm{kg\,mol^{-1}}$, $Đ = 3.7$) to be 1.28 eV in ODCB solution (Figure 1 a), which is smaller than the 1.36 eV reported for the thiophene analogue PDPP3T ($M_n = 54\ \mathrm{kg\,mol^{-1}}$, $Đ = 3.15$).[20]

From cyclic voltammetry measurements, the onsets of oxidation and reduction of PDPPTe2T ($M_n = 23.2\ \mathrm{kg\,mol^{-1}}$, $Đ = 3.7$) in a thin film were found at 0.30 and −1.17 V vs Fc/Fc^+ (SI), corresponding to HOMO and LUMO energy levels at −5.40 and −3.93 eV vs vacuum, respectively. The electrochemical bandgap of PDPPTe2T was calculated as 1.47 eV which is smaller than the 1.56 eV bandgap reported for PDPP3T,[20] though this latter value was measured in solution and not in a thin film.

In order to compare the *ipso*-arylative polymerization approach to the widely used Stille and Suzuki–Miyaura methods, we attempted polymerization of appropriate tellurophene derivatives (**7** and **8**) with monomer **2** by these two methods under similar conditions (SI). It is difficult to make a fair comparison between these polymerization methods because of method-necessitated changes in polymerization conditions: different palladium sources and ligands ($Pd(OAc)_2$ with PCy_3 or $Pd(PPh_3)_4$) are used since $Pd(OAc)_2$ with PPh_3 often generates *ortho*-arylated products as well as *ipso*-arylated products,[17] different solvents are required depending on polymerization methods (*o*-xylene for *ipso*-arylative polymerization, toluene for Stille polymerization and toluene/water for Suzuki polymerization), and only high molecular-weight (chloroform-insoluble) fractions were analyzed.

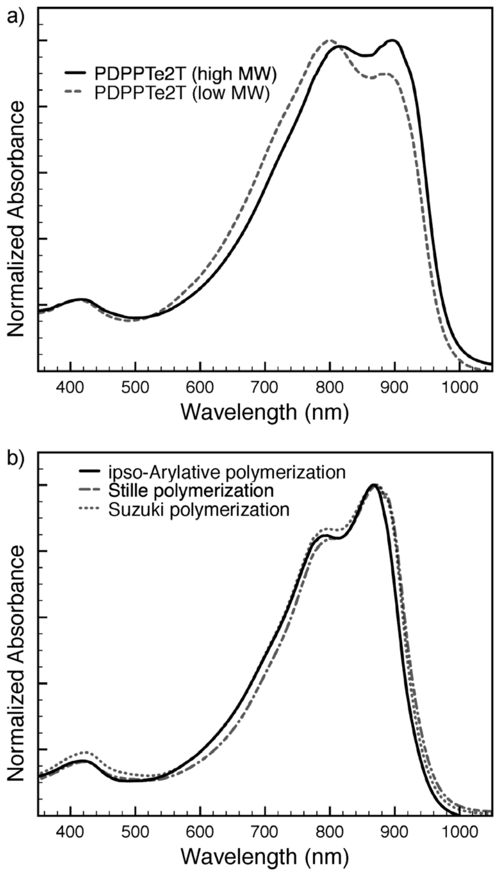


Figure 1. Optical absorption spectra of PDPPTe2T synthesized by a) *ipso*-arylative polymerization in ODCB and b) *ipso*-arylative, Stille, and Suzuki polymerizations in chloroform.

Molecular weights of polymers were obtained as $M_n = 25.1\ \mathrm{kg\,mol^{-1}}$ (PDI = 3.5) for Stille and $M_n = 25.9\ \mathrm{kg\,mol^{-1}}$ (PDI = 2.7) for Suzuki polymerization, respectively. Optical absorption spectra of PDPPTe2T obtained from three different polymerization methods showed similar relative intensities of two absorption maxima (I_1/I_0 in Figure S2) and absorption edges, indicating that all the polymerization methods tested are synthetically efficient protocols (Figure 1b).

To understand how substitution of tellurium for sulfur in the conjugated heterocyclic backbone of the polymer affects materials properties, photovoltaic characteristics were investigated for bulk heterojunction (BHJ) solar cells containing PDPPTe2T (low- and high-molecular weight portions) prepared by *ipso*-arylative polymerization as the electron donor and [6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) as the electron acceptor (device structure: indium tin oxide (ITO)/MoO_x (9 nm)/PDPPTe2T:$PC_{71}BM$/LiF (1 nm)/Al). PDPPTe2T/$PC_{71}BM$ weight ratios from 1:1 to 1:4 were examined. Current density–voltage (*J*–V) characteristics from the optimized devices under simulated air mass 1.5 global (AM 1.5G) irradiation at $100\ \mathrm{mW\,cm^{-2}}$ are shown in Figure 2a and summarized in Table 2. Devices processed solely from chloroform generated a low photocurrent ($J_{sc} = 0.64\ \mathrm{mA\,cm^{-2}}$, SI). The use of 1-chloronaphthalene as a processing additive[21] improved the device performance substantially by increasing photocurrent ($J_{sc} = 10.0\ \mathrm{mA\,cm^{-2}}$, SI), whereas thermal annealing (150 °C, 10 min) deteriorated performance. It is interesting to note similar improvements could be achieved by casting active layers from mixtures of chloroform and ODCB.[18]

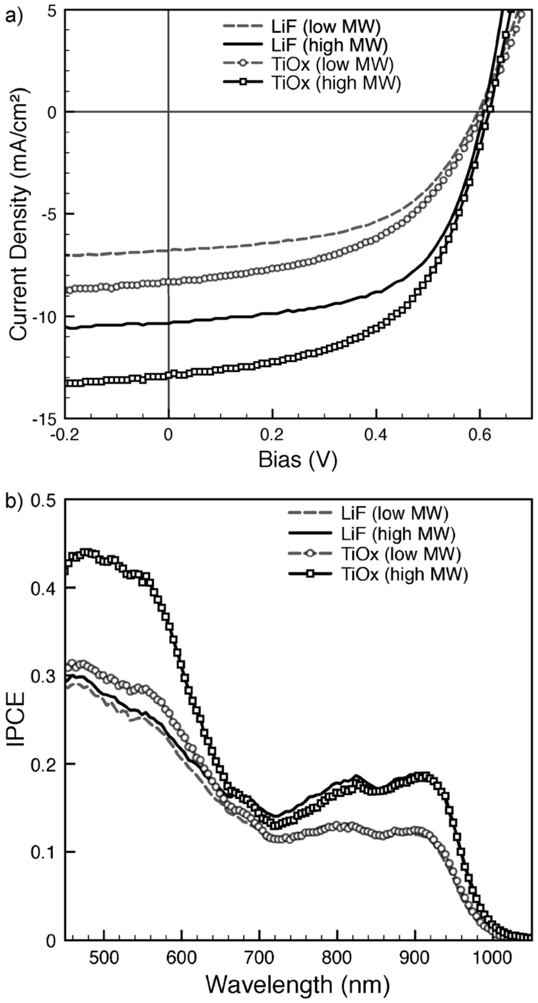


Figure 2. a) *J–V* curves and b) IPCE measurements for solar cells prepared from PDPPTe2T. Device structure: indium tin oxide (ITO)/MoO_x/PDPPTe2T:$PC_{71}BM$/LiF or TiO_x/Al.

Table 2: Solar cell device parameters.

PDPPTe2T	Cathode interlayer	V_{oc} [V]	J_{sc} [$\mathrm{mA\,cm^{-2}}$]	FF	PCE [%] max	avg ± std
Low MW[a]	LiF	0.59	6.6	0.55	2.2	2.08 ± 0.08
	TiO_x	0.60	8.3	0.50	2.5	2.44 ± 0.05
High MW[b]	LiF	0.60	10.4	0.60	3.7	3.63 ± 0.10
	TiO_x	0.61	12.9	0.56	4.4	4.14 ± 0.19

[a] $M_n = 8.0\ \mathrm{kg\,mol^{-1}}$ (PDI = 3.81). [b] $M_n = 23.2\ \mathrm{kg\,mol^{-1}}$ (PDI = 3.67). [c] All PCEs were averaged over 9 devices.

Blends of high- and low-molecular weight portions of PDPPTe2T with $PC_{71}BM$ at a 1:3 weight ratio (PDPPTe2T:$PC_{71}BM$) cast from a mixture of chloroform and ODCB (4:1, v/v) resulted in the best performing devices with measured PCEs of 3.7 % (high molecular weight) and

2.2% (low molecular weight), respectively. Incident photon conversion efficiency (IPCE) measurements showed that the onsets of photocurrents from PDPPTe2T devices reached almost 1 μm (Figure 2b), reconfirming that the tellurium substitution indeed contributes to enhancing light harvesting at longer wavelengths than seen for PDPP3T which has a photoresponse up to 900 nm.[20] The superior performance from the device prepared from the high-molecular weight portion of PDPPTe2T can be attributed to the enhanced IPCE in the 700 to 950 nm range. This illustrates the importance polymer molecular weight can play in high efficiency solar cell materials.[22–25]

In order to further improve solar cell efficiencies, we used TiO_x, prepared by a solution-based sol–gel process, as an air-stable optical spacer and hole-blocking cathode interlayer,[26,27] instead of LiF. Higher PCEs of 4.4% and 2.5% were measured for the high and low molecular weight fractions in these devices, mainly as a result of an increase in J_{sc} (12.9 from 10.4 $mA\,cm^{-2}$ for the high molecular weight sample and 8.3 from 6.6 $mA\,cm^{-2}$ for low molecular weight samples) (Figure 2a and Table 2). These results are supported by superior quantum efficiencies for the TiO_x devices in the region of 450 to 650 nm (Figure 2b). Compared to PDPP3T-based PV cells, PDPPTe2T devices showed a comparable PCE (4.4 vs 4.7%) but a slightly enhanced J_{sc} (12.9 vs 11.8 $mA\,cm^{-2}$), though the PDPP3T device architecture (ITO/PEDOT:PSS/PDPP3T:$PC_{71}BM$/LiF/Al) differs enough that direct comparisons should be made with caution.[20]

To further elucidate the effect of substituting tellurium (PDPPTe2T) for sulfur (PDPP3T) on the observed optoelectronic properties at the molecular level, we performed density functional theory (DFT) and time-dependent DFT (TDDFT) calculations on model oligomers of PDPPTe2T and PDPP3T with finite chain lengths ($n = 2$, 4, and 6). In all molecules, 2-hexyldecyl side chains were replaced with methyl groups for simplicity and full geometry optimization was performed with the repeating unit as shown in SI to examine the molecular structure and the optical bandgap. All molecules maintain backbone planarity and the electronic distributions of the frontier orbitals for PDPPTe2T and PDPP3T are very similar (Figure 3; full orbital descriptions are shown in the SI). Nonetheless, there are some small differences. Tellurium has no contribution to the highest occupied orbital (HOMO), while sulfur contributes. On the other hand, tellurium contributes slightly more to the lowest unoccupied orbital (LUMO) than sulfur. The calculated bond lengths display some subtle differences, too. Most importantly, the carbon–carbon bond lengths between tellurophene and thiophene rings in PDPPTe2T are calculated to be shorter (1.433 Å) than those between thiophene rings (1.438 Å) in the same positions in PDPP3T. This can be interpreted as resulting from an increased contribution of the quinoid form to the frontier orbitals of PDPPTe2T.[28] As a consequence, the HOMO level is higher in PDPPTe2T than in PDPP3T, while the LUMO level is lower, even though electronic distributions of the frontier orbitals do not appear to differ significantly between PDPPTe2T and PDPP3T (SI).

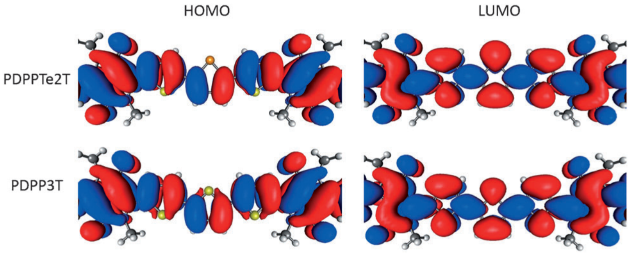


Figure 3. Calculated frontier orbitals of PDPPTe2T (top) and PDPP3T (bottom) oligomers.

TDDFT calculations of the optical bandgaps verify this conclusion. For every chain length, the first excitation energy for PDPPTe2T is consistently lower than that for PDPP3T. We estimate the optical gap at infinite chain length to be 1.14 eV for PDPPTe2T and 1.24 eV for PDPP3T, in good agreement with optical absorption spectra (SI). Together, the calculations suggest that the replacement of one thiophene in a terthiophene group with a tellurophene can make a significant impact on the optoelectronic characteristics of a polymer.

In conclusion, we have synthesized a tellurophene-containing donor–acceptor type low-bandgap polymer by palladium-catalyzed *ipso*-arylative polymerization. PDPPTe2T/$PC_{71}BM$ bulk heterojunction photovoltaic devices—the first reported PV devices prepared from tellurophene-containing polymers—reached PCEs of 4.4%. IPCE measurements on these devices show that atomic substitution from sulfur to tellurium causes a red-shift in absorption and enables donor materials to collect photocurrent up to 1 μm. In this study, we reconfirmed that the molecular weights of polymers play important roles in obtaining high PCE solar cell devices.[19,20,22] Currently, we are in the process of side chain modification to further improve polymer solubility, which limits the molecular weights that can be obtained during synthesis. We are working to generalize this palladium-catalyzed polymerization method and to apply this methodology toward the synthesis of new polymer systems for high efficiency solar cell materials.

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Keywords: *ipso*-arylative polymerization · low-bandgap polymers · microwave-assisted reactions · organic solar cells · tellurophene

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