ORGANIC
LETTERS

2013
Vol. 15, No. 5
1032–1035

Efficient Synthesis of Dithienogermole (DTG) Derivatives via Olefin Cross-Metathesis

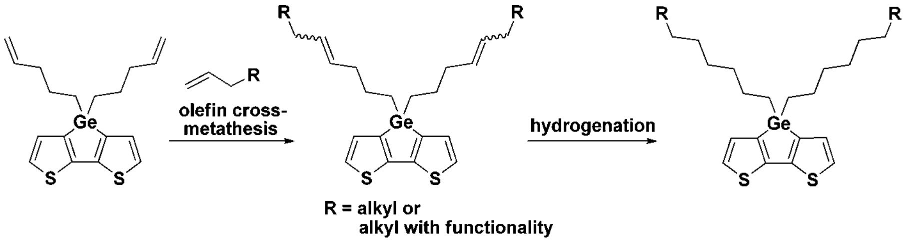
Kyukwan Zong,[‡] James J. Deininger,[†] and John R. Reynolds*[,†]

*School of Chemistry and Biochemistry, School of Materials Science and Engineering,
Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta,
Georgia 30332-0400, United States, and Institute of Fusion Science, Department of
Chemistry Education, Division of Science Education, Chonbuk National University,
Jeonju, Jeonbuk 561-756, Republic of Korea*

kzong@jbnu.ac.kr; reynolds@chemistry.gatech.edu

Received December 24, 2012

ABSTRACT



4,4′-Bis-(4-pentenyl)-dithieno[3,2-*b*:2′,3′-*d*]germole was synthesized as a functional building block for the efficient preparation of dithienogermole (DTG) derivatives with varying alkyl chain lengths and pendant functionalities in excellent yields. These derivatives were efficiently isolated via olefin cross-metathesis followed by hydrogenation.

Semiconducting copolymers containing dithienosilole (DTS) and dithienogermole (DTG) donors have attracted attention due to their utility in synthesizing molecules and polymers potentially useful in organic electronic applications, such as organic photovoltaics (OPVs)[1] and organic field effect transistors (OFETs).[2]

As shown in Figure 1, DTG is analogous in structure to cyclopentadithiophene (CPDT) and DTS where the carbon or silicon atom is substituted with germanium respectively.

In comparison with the C and Si atoms employed in CPDT or DTS, it has been reported that the bridging Ge atom in DTG[3] can result in an enhancement in intermolecular ordering, due to the long C−Ge bond lengths, moving the bulky side chains away from the planar heterocycle allowing stronger π−π stacking.[3b] As shown in Figure 2, the copolymer between 4,4′-bis(2-ethylhexyl)dithieno[3,2-*b*:2′,3′-*d*]germole and 2,1,3-benzodithiazole (BTD) exhibits an FET mobility[3h] up to 0.11 cm^2 V^{-1} s^{-1} while the copolymer with *N*-octylthieno[3,4-*c*]pyrrole-4,6-dione (TPD) has given solar cell AM 1.5 power conversion efficiencies (PCEs) up to 7.3%, higher than the corresponding

---

[‡] Chonbuk National University.

[†] Georgia Institute of Technology.

(1) (a) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324–1338. (b) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58–77. (c) Kippelen, B.; Brédas, J.-L. *Energy Environ. Sci.* **2009**, *2*, 251–261. (d) Dennler, G.; Scharber, M. C.; Brabec, C. J. *Adv. Mater.* **2009**, *21*, 1323–1338. (e) Boudreault, P.-L. T.; Najari, A.; Leclerc, M. *Chem. Mater.* **2011**, *23*, 456–469. (f) Zhou, H.; Yang, L.; You, W. *Macromolecules* **2012**, *45*, 607–632.

(2) (a) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *281*, 1741–1744. (b) Forrest, S. R. *Nature* **2004**, *428*, 911–918. (c) Locklin, J.; Roberts, M.; Mannsfeld, S.; Bao, Z. *Polym. Rev.* **2006**, *46*, 79–101. (d) Zaumseil, J.; Sirringhaus, H. *Chem. Rev.* **2007**, *107*, 1296–1323.

(3) For recent papers on copolymers containing DTG, see: (a) Ohshita, J.; Hwang, Y.-M.; Mizumo, T.; Yoshida, H.; Ooyama, Y.; Harima, Y.; Kunugi, Y. *Organometallics* **2011**, *30*, 3233–3236. (b) Amb, C. M.; Chen, S.; Graham, K. R.; Subbiah, J.; Small, C. E.; So, F.; Reynolds, J. R. *J. Am. Chem. Soc.* **2011**, *133*, 10062–10065. (c) Hwang, Y.-M.; Ohshita, J.; Harima, Y.; Mizumo, T.; Ooyama, Y.; Morihara, Y.; Izawa, T.; Sugioka, T.; Fujita, A. *Polymer* **2011**, *52*, 3912–3916. (d) Gendron, D.; Morin, P.-O.; Berrouard, P.; Allard, N.; Aïch, B. R.; Garon, C. N.; Tao, Y.; Leclerc, M. *Macromolecules* **2011**, *44*, 7188–7193. (e) Fei, Z.; Kim, J. S.; Smith, J.; Domingo, E. B.; Anthopoulos, T. D.; Stingelin, N.; Watkins, S. E.; Kim, J.-S.; Heeney, M. *J. Mater. Chem.* **2011**, *21*, 16257–16263. (f) Small, C. E.; Chen, S.; Subbiah, J.; Amb, C. M.; Tsang, S.-W.; Lai, T.-H.; Reynolds, J. R.; So, F. *Nat. Photonics* **2012**, *6*, 115–120. (g) Fei, Z.; Kim, Y.; Smith, J.; Domingo, E. B.; Stingelin, N.; McLachlan, M. A.; Song, K.; Anthopoulos, T. D.; Heeney, M. *Macromolecules* **2012**, *45*, 735–742. (h) Kim, J. S.; Fei, Z.; James, D. T.; Heeney, M.; Kim, J.-S. *J. Mater. Chem.* **2012**, *22*, 9975–9982. (i) Nicolas, A.; Aïch, R. B.; Gendron, D.; Boudreault, P.-L. T.; Tessier, C.; Alem, S.; Tse, S.-C.; Tao, Y.; Leclerc, M. *Macromolecules* **2010**, *43* (5), 2328–2333.

10.1021/ol303529w

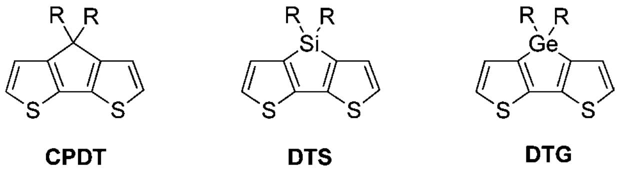


Figure 1. Structures of common fused systems used as donor moieties.

DTS polymer.[3b] Using an inverted cell morphology with interface control, DTG-TPD based polymer solar cells have been prepared with PCEs up to 8.5% (7.4% certified power conversion efficiency).[3f]

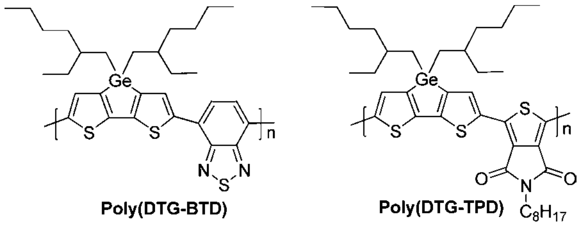


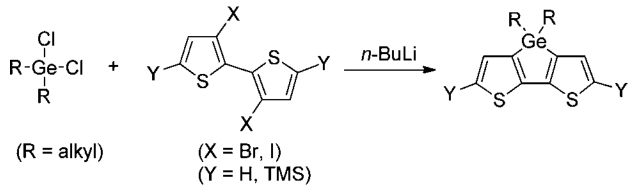
Figure 2. Polymer repeat unit structures for DTG-based materials with BTD and TPD acceptors employed in organic electronics and solar cells.

In order to prepare sufficiently soluble DTG-based polymers for effective processing, relatively long chain alkyl solubilizing groups are required on the bridging germanium atom. To date, the alkyl chains on DTG reported in the literature have been limited to 2-ethylhexyl, *n*-butyl, and methyl. One reason for this is due to the fact that while the dichlorodimethyl-, dichlorodiethyl-, and dibutyldichloro-germane intermediates are commercially available, others such as dichlorodiethylhexylgermane are not. Due to the synthetic complexity of preparing long chain dialkyldichlorogermane derivatives, it has been a challenge to synthesize multiple DTG derivatives.

The DTG core is generally constructed by reacting the 3,3′-dilithiated-2,2′-bithiophene (**2**) with a dialkyl-dichlorogermane (**1**) as shown in Scheme 1.[3a,b,d] The longer alkyl derivatives, such as 2-ethylhexyl, are prepared from the reaction of $GePh_2Cl_2$ or $GeCl_4$ with the corresponding alkyl Grignard or alkyl lithium reagents.[3i] However, as the alkyl chain length becomes longer, the preparation of the organometallic reagents becomes difficult due to their lack of reactivity toward the magnesium or lithium metals.

Another challenge in the preparation of long chain dialkyldichlorogermanes lies in the purification, as they are generally isolated as oils by fractional vacuum distillation and are sensitive to moisture. As such, as the molecular weight of the compound increases, distillation becomes exceedingly difficult. Thus, in order to overcome these synthetic obstacles, we envisioned the synthesis of a single precursor compound, which can be easily manipulated in order to produce various DTG derivatives as illustrated in Scheme 2. This synthetic strategy eliminates the required isolation of a separate dialkyldichlorogermane for every new DTG derivative produced.

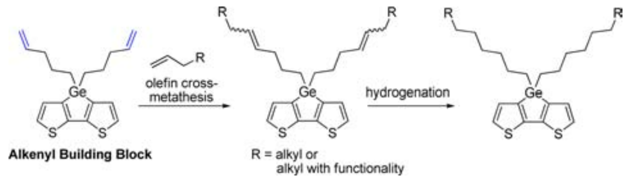
Scheme 1. General Synthetic Route for Construction of DTG Core



In this study, DTG functionalized with terminal pentenyl chains on Ge (Scheme 3) was designed as a synthetic "building block" compound, as the terminal alkenyl group can be further functionalized via olefin cross-metathesis in order to install a variety of alkyl chains and further incorporate functionality including halides and esters.

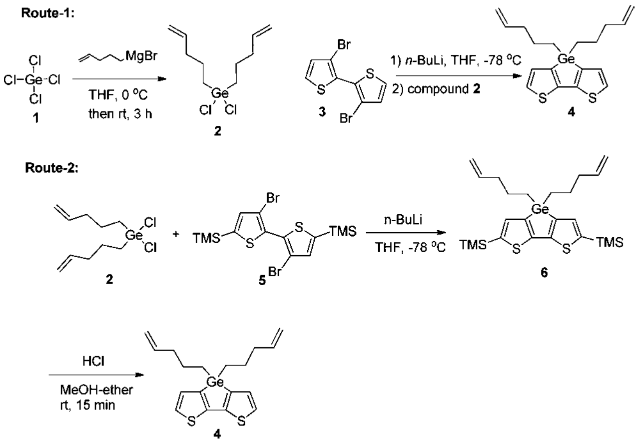
For the preparation of **4**, 4-pentenylmagnesium bromide was prepared from magnesium and 4-pentenyl bromide and subsequently added to $GeCl_4$ by a slight modification of the published procedure (see Supporting Information), as illustrated by Scheme 3.[3b] This reaction usually results in a mixture of several products (mono-, di-, and trisubstituted), yet the major fraction, dichloro-di-4-pentenylgemane (**2**), could be isolated by fractional distillation under reduced pressure in a 40−45% yield. To enhance product formation from starting reagents, the lowest boiling 4-pentenyltrichlorogermane fraction could be isolated and recycled for the preparation of **2**. Freshly distilled dichloro-di-4-pentenylgermane was added to 3,3′-dilithiated-2,2′-bithiophene prepared from 3,3′-dibromo-2,2′-bithiophene and *n*-BuLi at −78 °C to give 4,4′-bis-(4-pentenyl)-dithieno-[3,2-*b*:2′,3′-*d*]germole (**4**) in 52% yield (Route 1).

Scheme 2. Synthetic Strategy for Various DTG Derivatives from an Alkenyl Building Block Compound

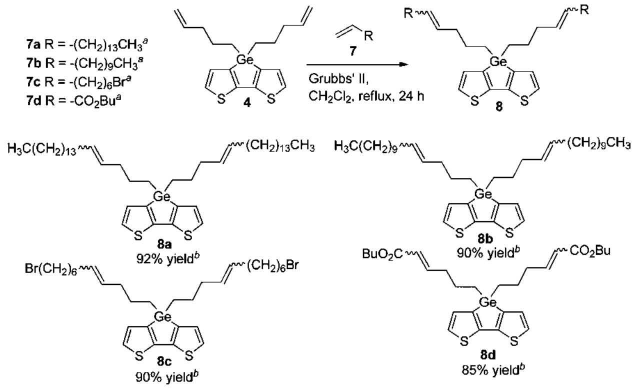


We subsquently explored the use of 2,2′-TMS functionalized bithiophene (**5**) in order to improve the yield by avoiding possible side reactions at the terminal 2,2′-positions of bithiophene. The reaction of **2** with dilithiated **5** at −78 °C gave **6** in 65% yield. Subsequently, **6** was easily converted into **4** in 80% yield by stirring in 5% HCl solution in MeOH/ether for 10 min

Scheme 3. Synthesis of 4,4′-Bis-(4-pentenyl)-dithieno-[3,2-*b*:2′,3′-*d*]germole as a Building Block Compound



Scheme 4. Synthesis of DTG Derivatives from Olefin Cross-Metathesis



[a] 16 equiv of alkenes were used.

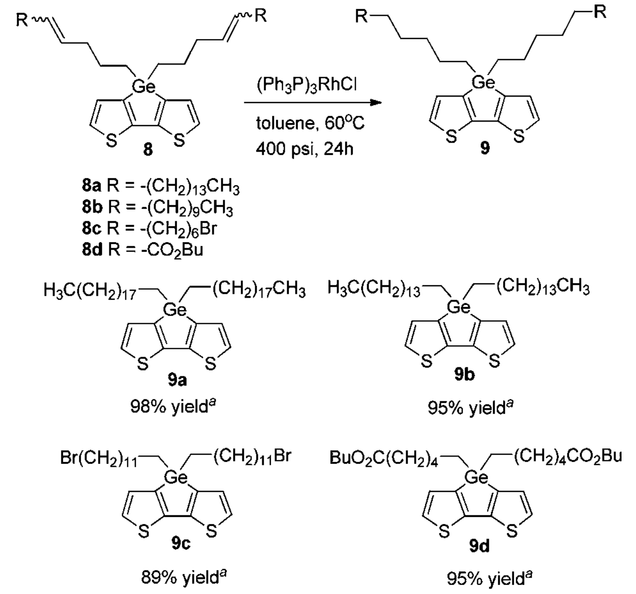
[b] Isolated yields reported as a mixture of *cis* and *trans* isomers.

(Route 2). Although the latter route yielded **4** in an overall yield of 52%, it does require the additional step of TMS deprotection.

With **4** in hand, we explored the installation of extended alkyl chains and further functionalities by employing olefin cross-metathesis as shown in Scheme 4.[4] The competition between ring closing or cross-metathesis is known to be highly dependent upon the ratio of two alkenes employed. In order to minimize ring closure, or dimerization by self-metathesis and, thus, maximize the product by cross-metathesis, the ratio of **4** and **7** were closely examined and the optimal conditions were found to include use of an $\sim$16-fold excess of **7**. The reaction of **4** with 16 equiv of 1-hexadecene (**7a**) under standard metathesis conditions gave **8a** in 92% yield. As expected, the products were composed of a mixture of *trans*−*trans*, *trans*−*cis*, and *cis*−*cis* isomers, which were inseparable by column chromatography on silica gel. The separation of these isomers is not necessary due to the fact that the double bonds are saturated in the next step. Similarly, the reaction of **4** with 1-dodecene (**7b**) yielded **8b** in 90% yield. In addition, cross-metathesis of **4** with alkenes having functionality, such as 8-bromooct-1-ene (**7c**) or butyl acrylate (**7d**), worked as well to give **8c** or **8d** in excellent yields.

Hydrogenation of the products obtained from cross-metathesis was investigated under several reaction conditions as shown in Scheme 5. Utilization of a hydrogen balloon in the presence of 5% or 10% Pd/C at ambient or elevated temperature was not successful. In these cases, the reactions gave a distribution of fully saturated, partially saturated, and unsaturated products as judged by TLC. Therefore, high pressure hydrogenation was carried out in the presence of Pd/C or Wilkinson's catalyst under various pressures and temperatures.[5] Optimal conditions for hydrogenation were achieved under 400 psi of hydrogen in the presence of 10 mol% Wilkinson's catalyst. Under these conditions, the reaction proceeded smoothly to afford fully saturated DTG derivatives in excellent yields as shown in Scheme 5.

Scheme 5. Hydrogenation of **8** and Isolated Yields



[a] Isolated yields.

In conclusion, we report a new efficient synthetic route that allows access to various DTG derivatives using olefin cross-metathesis as a key step. Terminally alkenylated DTG (**4**) serves as an easily accessed precursor for olefin cross-metathesis with various alkenes to yield unsaturated products with additional functionalities. Hydrogenation of these products afforded saturated DTG derivatives in excellent yields. The ability to access long alkyl chains, or

---

(4) Chatterjee, A. K.; Choi, T.-L.; Sanders, D. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 11360–11370.

(5) Sworen, J. C.; Wagener, K. B. *Macromolecules* **2007**, *40*, 4414–4423.

variously functionalized DTGs, opens up new possibilities for synthesizing previously difficult to prepare donor materials for the organic electronic fields of OPV and OFETs, among others. The concepts reported herein can be extended to syntheses of many of the long chain and functional group modified fused systems employed in organic electronics, such as the CPDT, DTS, and dithienopyrrole (DTP), along with organoboroles and organophospholes.

Acknowledgment. This work was partially supported by the Office of Naval Research (N00014-10-1-0454) along with research funds from Chonbuk National University.

Supporting Information Available. Synthetic procedures and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.