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Synthesis and Photovoltaic Properties of Poly(dithieno[3,2-*b*:2′,3′-*d*]germole) Derivatives

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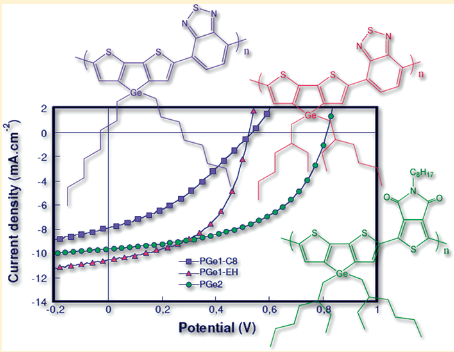
Supporting Information

ABSTRACT: A series of new dithieno[3,2-*b*:2′,3′-*d*]germole copolymers have been synthesized and characterized. The dithienogermole unit has been polymerized with different aromatic comonomers such as the benzothiadiazole (**PGe1-C8** and **PGe1-EH**) and thieno[3,4-*c*]pyrrole-4,6-dione (**PGe2**). Suzuki and Stille coupling polymerizations under various conditions have been utilized. The polymers were then characterized by size-exclusion chromatography and thermal analyses (TGA, DSC), and their optical and electronic properties were investigated by UV−vis absorption spectroscopy and cyclic voltammetry. These low bandgap polymers (1.3−1.7 eV) have also been tested for photovoltaic applications; the best result was achieved with polymer **PGe2**, which shows a power conversion efficiency of 4.1%.



INTRODUCTION

Harvesting energy directly from the sun is one of the most important methods to address the world energy need. Plastic solar cell possesses many advantages over the silicon-based devices such as a lower manufacturing cost, an easy printing, and flexibility of the devices.[1] Organic photovoltaic devices are usually made of conjugated polymers whose absorption spectrum can be fine-tuned to match the solar absorption spectra. Recently, a few devices made with conjugated polymers have shown a power conversion efficiency (PCE) over 7% when blended with fullerene derivatives.[2] These polymers are composed of a dithienosilole,[3] a benzothiadiazole,[4] or a thieno[3,4-*c*]-pyrrole-4,6-dione[5,6] unit. Also, new materials with PCEs over 8% have been reported from Solarmer, Konarka, Heliatek, and Mitsubishi,[7] but no indications of the structure have been revealed.

In parallel, the group of Bazan has compared cyclopenta-[2,1-*b*;3,4-*b*′]dithiophene and dithieno[3,2-*b*;2′,3′-*d*]silole-based copolymers.[8] They observed that the modification of the bridging carbon atom by a silicon atom has a direct effect on the morphology of the polymer/PCBM blends which ultimately influences the polymer chain packing in the solid state. Indeed, studies done by Brabec's and Yang's groups[9,10] concluded that replacing the carbon atom by the silicon atom enhances the crystallinity of the material. Along these lines, it could then be interesting to evaluate the influence of a germanium atom. The chemistry of group 14 metalloles has been reviewed[11,12] in the past, and many papers have been reported on the synthesis of sila- and germacyclopentadiene derivatives.[13−17] Also, crystallographic data of some organometallic compounds such as 1,1-diethynyl-2,3,4,5-tetraphenylgermole or 9-germafluorenyl have also been investigated.[18−21] To summarize, those papers show that the C−Ge bond length is longer than the C−Si bond. Thus, it should remove the alkyl side chain from the heterocyle and allow better $\pi-\pi$ interchain interactions. Also, a work by Tamao et al. reports the effect of group 14 metalloles on their electronic structure. On model compounds, they observe that the silole, the germole, or the stannole derivatives have similar electronic structure and comparable photophysical properties such as similar bandgaps and LUMO and HOMO energy levels.[22]

However, up to now, germoles have received limited attention as building blocks for π-conjugated systems. For instance, only some poly(germafluorene)s[23−25] and poly(dithienogermole)s[27] have been recently investigated for plastic electronics. Yet, during the preparation of this article, Reynolds et al. have reported the use of a poly(dithienogermole) in photovoltaic devices.[28] After optimization of the devices, they were able to reach a PCE of 7.3%. This result clearly emphasizes the interest to gain a better knowledge of such derivatives. Consequently, a series of three dithieno[3,2-*b*;2′,3′-*d*]germole-based copolymers have been synthesized and characterized. Comonomer units such as the benzothiadiazole and the thieno[3,4-*c*]pyrrole-4,6-dione have been utilized. Different polymerization methods have been investigated. Finally, this work reports the use of these poly(dithienogermole) derivatives in photovoltaic devices.

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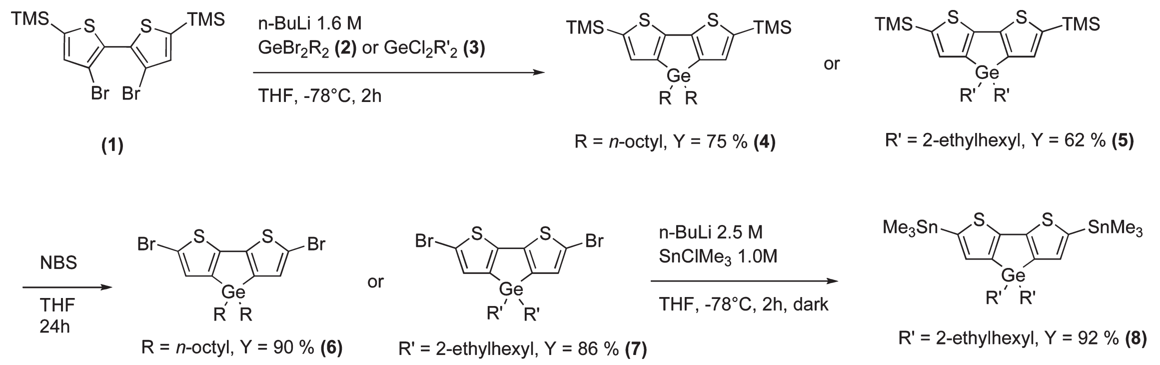
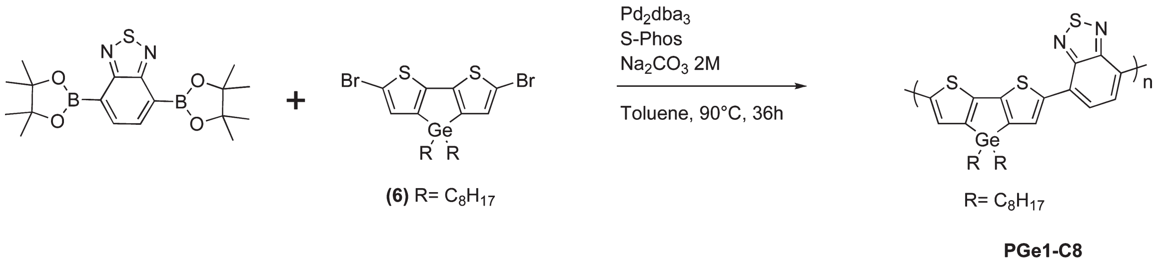
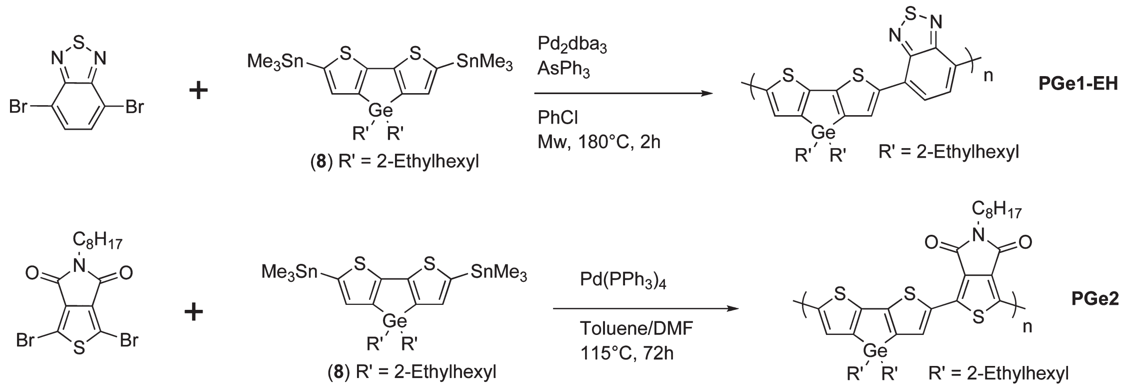
Scheme 1. Synthesis of the Dithienogermole Monomers 6 and 8



Scheme 2. Polymerization of PGe1-C8



Scheme 3. Polymerization of PGe1-EH and PGe2



■ SYNTHESIS OF THE MONOMERS

The synthetic pathways of monomers **6** and **8** are shown in Scheme 1. First, compound **1** was prepared as reported in the literature.[29,30] Then, under strict Schlenk conditions, a reaction with *n*-butyllithium 1.6 M at −78 °C followed by the addition of the germane derivative[23] (**2**) generated the 4,4′-bis(octyl)-5,5′-bis(trimethylsilyl)dithieno[3,2-*b*:2′,3′-*d*]germole (**4**) in 75% yield. Monomer **6** is then obtained with a yield of 90% from a bromination reaction using *N*-bromosuccinimide (NBS) in THF. To obtain compound **7**, the same procedure is used as for compound **6**, but with a different germane derivative[26] (**3**). Then, the bromine atoms are replaced by trimethylstannyl groups. This reaction is performed with the use of *n*-BuLi and Me_3SnCl to give compound **8** in good yield (92%). Compound **8** is light-sensitive and should be kept in the dark. Also, no purification such as column chromatography was performed as it accelerated the degradation of the tin derivatives. Two different alkyl chains were used on the germanium atom (**6** and **8**) to compare the effect on the solubility of the resulting polymers. All compounds were characterized by ^{1}H and ^{13}C NMR. For more details, see the Supporting Information.

■ SYNTHESIS OF THE POLYMERS

Three polymers were synthesized according to Schemes 2 and 3. First, a Suzuki coupling polymerization of monomer **6** with the 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) comonomer gave polymer **PGe1-C8.** Conditions for the polymerization are reported in Scheme 2. After analysis, it seems that the presence of linear octyl chains on the dithienogermole moiety

Table 1. Physical and Electronic Properties of Polymers PGe1-C8, PGe1-EH, and PGe2

polymer	M_n, kg/mol	PDI	T_g, °C	T_d, °C	E_{HOMO},[a] eV	E_{LUMO},[a] eV	E_g^{elec}, eV	E_g^{opt}, eV
PGe1-C8	8.9	1.9	–	420	−5.21	−3.85	1.36	1.33
PGe1-EH	12.4	1.7	–	420	−5.22	−3.93	1.29	1.43
PGe2	16.3	1.9	–	440	−5.66	−3.93	1.73	1.67

[a] Versus SCE.

greatly limits the solubility of the polymers as we obtained low molecular weights. This is one of many factors (monomer purity, reaction time, solubility, etc.) that can affect the molecular weight. Different conditions were also investigated such as the use of bases (K_2CO_3, Cs_2CO_3, Bu_4NOH 20%) and catalysts ($Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, $Pd(OAc)_2$) with various reaction times (8−72 h). Unfortunately, lower polymerization yields and molecular weights were obtained with those last conditions. Finally, the polymer was purified by Soxhlet extractions (methanol, acetone, hexanes, and chloroform). ^{1}H NMR analysis shows peaks between 0.87 to 1.57 and 2.10 ppm for the protons of the alkyls chains and peaks at 7.85 and 8.19 ppm, which correspond to the signal of the aromatic protons. The number of aromatic and aliphatic protons estimated from integration of the peaks is consistent with the expected repeating unit of the copolymer.

Second, two other polymer derivatives, **PGe2** and **PGe1-EH**, were obtained. To enhance the solubility of the polymers, we decided to use 2-ethylhexyl side chains instead of *n*-octyl chains on the dithienogermole moiety. This enhanced solubility should also increase the molecular weights. Polymer **PGe2** was obtained by a Stille coupling between monomer **8** and the thieno[3,4-*c*]pyrrole-4,6-dione unit using $Pd(PPh_3)_4$ as the catalyst in a mixture of toluene/DMF (see Scheme 3). To further increase the molecular weights, **PGe1-EH** was synthesized by a microwave polymerization[31] of monomer **8** and the 4,7-dibromo-2,1,3-benzothiadiazole comonomer using $Pd_2(dba)_3$, $AsPh_3$, and chlorobenzene as the system conditions. Indeed, the groups of Bazan and Coffin have used those conditions to obtain higher molecular weights on similar materials.[8,32] After purification by Soxhlet extractions and removal of the metals catalysts, the polymers were characterized as described below.

MOLECULAR WEIGHTS

All polymers were characterized by size-exclusion chromatography (SEC) based on monodisperse polystyrene standards in 1,2,4-trichlorobenzene at 140 °C. Number-average-molecular weights obtained for the present polymers are reported in Table 1. The analysis shows a number-average molecular weight (M_n) of 8.9 kg/mol with a polydispersity index (PDI) of 1.9 for polymer **PGe1-C8**. These moderate molecular weights can be explained by the choice of the alkyl side chain on the germanium atom. Indeed, the straight *n*-octyl chain seems to limit the solubility of the polymer. For example, **PGe1-EH** and **PGe2**, which possess 2-ethylhexyl side chains, have reached higher molecular weights. Polymer **PGe1-EH**, which has been polymerized by microwave irradiation, exhibits slightly higher molecular weights (12.4 kg/mol, PDI of 1.7; see Table 1) compared to polymer **PGe1-C8**. Even by using the microwave-assisted method reported by Bazan et al.[8] and by changing the reaction conditions such as the time, the catalyst, the solvent, and the ligand, we were not able to get higher molecular weights. It is possible that the relative purity of the tin derivative limits the molecular weights. Unfortunately, as mentioned earlier, attempt to purify the tin monomer results in degradation of the compound. However, a successful way to purify the tin monomer would be to use reverse-phase preparative HPLC as noted by Reynolds et al.[28] Finally, following a reported polymerization procedure for a similar material,[3] polymer **PGe2** has reached a number-average molecular weight of 16 kg/mol with a PDI of 1.9. For further details concerning the polymerization conditions, see the Supporting Information.

THERMAL AND OPTICAL PROPERTIES

To evaluate the thermal stability and the thermal transitions, thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) measurements were carried out for all the materials. Data are reported in Table 1. First, the TGA measurements show a thermal stability under nitrogen over 400 °C for all polymers. However, DSC experiments show no signs of thermal transitions such as glass or melting transitions. Nevertheless, the polymers show good solubility in organic solvents such as chloroform ($CHCl_3$), tetrahydrofuran (THF), or 1,2-dichlorobenzene (ODCB).

UV−vis absorption spectrum for all polymers in both solution and solid state are reported in Figure 1. First, polymer **PGe1-C8** shows two absorption bands at 417 and 690 nm in solution. In the solid state, the two absorption bands shifts to 426 and 777 nm, respectively. The optical bandgap (E_g^{opt}) in the solid state is determined at the absorption onset and is found to be 1.33 eV. This very low bandgap value is similar to the values reported in the literature for the dithieno[3,2-*b*:2′,3′-*d*]silole (1.37 eV) or cyclopentadithiophene (1.25 eV) polymeric derivatives.[8,29] Polymer **PGe1-EH**, which has a 2-ethylhexyl side chain instead of *n*-octyl, shows a very similar spectrum to **PGe1-C8** in solution, as the alkyl chain modification has little effect on the absorption bands (417 and 691 nm). Nevertheless, in the solid state, the optical bandgap for **PGe1-EH** is slightly higher (1.43 eV) compared to **PGe1-C8** (1.33 eV). Indeed, the solid-state optical properties of polymer **PGe1-EH** seem to be affected by the presence of 2-ethylhexyl side chains. Polymer **PGe2** shows an absorption maximum at 671 nm in solution and at 675 nm in the solid state. The bandgap calculated from the absorption onset is found to be 1.67 eV. This data is consistent with that obtained for the 4,4-bis(2-ethylhexyl)dithieno[3,2-*b*:2′,3′-*d*]silole−*N*-octylthieno[3,4-*c*]pyrrole-4,6-dione (PDTSTPD) system (1.73 eV).[3] Likewise, Reynolds's group have also estimated a similar bandgap of 1.69 eV on the exact same polymer.[28]

ELECTROCHEMICAL PROPERTIES

The HOMO and LUMO energy levels of all three polymers were determined by cyclic voltammetry. As shown in Figure 2, polymer **PGe1-C8** exhibits a quasi-reversible oxidation process and a nonreversible reduction process. Using the onset of the oxidation and the reduction process, the HOMO and LUMO

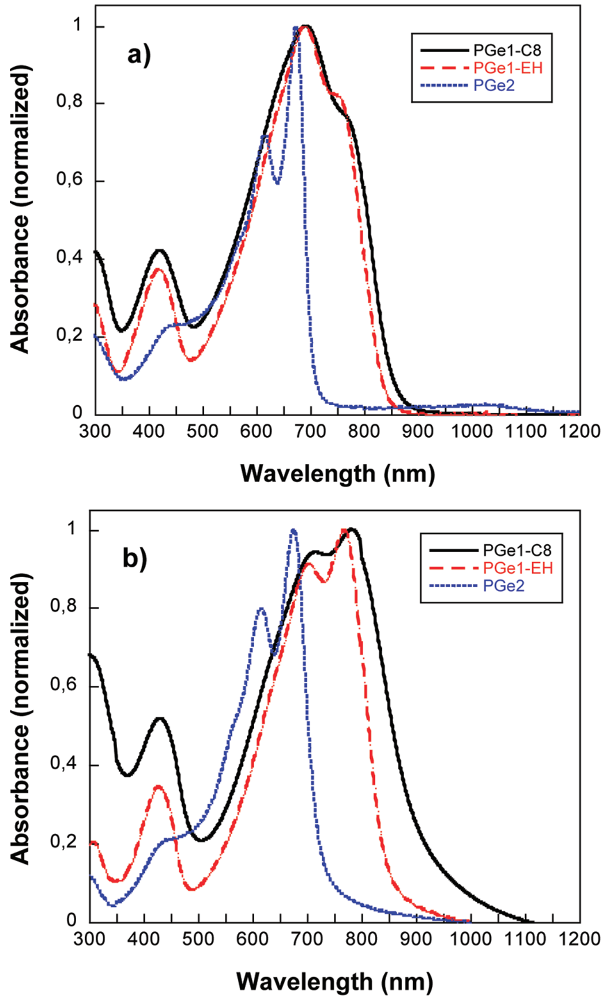


Figure 1. UV−vis absorption spectra of **PGe1-C8**, **PGe1-EH**, and **PGe2**: (a) solutions in chloroform; (b) films on glass substrates.

energy levels calculated are −5.21 and −3.85 eV, respectively. On the basis of the HOMO energy level, this polymer can be considered to be barely stable in air oxidation. Interestingly, the electrochemical bandgap E_g^{elec} (1.36 eV) deduced from the HOMO and LUMO energy levels is in good agreement with the optical bandgap E_g^{opt} (1.33 eV) and within the experimental errors. As for **PGe1-C8**, we observed a reversible oxidation process and a nonreversible process for polymer **PGe2** and **PGe1-EH**. The HOMO and LUMO energy levels, −5.22 and −3.93 eV, respectively, of polymer **PGe1-EH** are similar to those calculated for **PGe1-C8** (see Table 1). On the other side, the electrochemical bandgap for **PGe1-EH** (1.29 eV) is like the one obtained for **PGe1-C8** (1.36 eV), but lower compared to its own optical bandgap (1.43 eV). For the case of **PGe2**, the LUMO and HOMO energy levels are found to be −5.66 and −3.93 eV. On the basis of these values, the thieno[3,4-*c*]pyrrole-4,6-dione core seems to lower the HOMO energy level by 0.4 eV but keep the LUMO energy level almost the same as for polymer **PGe1-C8**. The electrochemical bandgap (E_g^{elec} = 1.73 eV) is relatively close to the optical bandgap (1.67 eV). These energy values are similar to those obtained for the PDTSTPD system (HOMO at −5.57 eV, LUMO at −3.88 eV, and E_g^{elec} at 1.69 eV).[3] For the same polymer (**PGe2**), Reynolds et al. have reported a similar HOMO at −5.60 eV, but a higher LUMO at −3.50 eV determined by cyclic voltammetry and differential pulse voltammetry.[28] Polymer **PGe2** should have a good air stability because its HOMO energy level is lower than the air oxidation threshold at −5.27 eV.[33] In brief, the modification of the alkyl side chains on the dithienogermole unit have little effect on the energy level properties but have more influence on the optical bandgap in solid state.

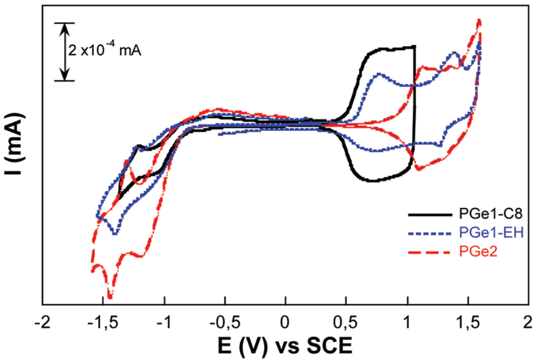


Figure 2. Cyclic voltammetry of polymers **PGe1-C8**, **PGe1-EH**, and **PGe2**.

Following most accepted models, to be efficient in a solar cell, a material must possesses a HOMO energy level between −5.2 and −5.8 eV and a LUMO energy level between −3.7 and −4.0 eV to ensure an air stability and a good charge transfer between the usual acceptor for solar cell devices such as PCBM.[34,35] Moreover, the bandgap must be within the range of 1.2−1.9 eV to match the maximum of the solar emission spectra.[36] On the basis of those criteria, the experimental data show that this new series of three dithieno[3,2-*b*;2′,3′-*d*]germane-based polymers should be good candidates for solar cell applications.

■ POLYMER SOLAR CELLS

To verify their potential for photovoltaic applications, bulk heterojunction solar cells were fabricated and tested. A conventional configuration (glass/ITO/PEDOT:PSS/polymer:$PC_{70}BM$/LiF/aluminum) was utilized. First, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer was spin-coated onto a precleaned ITO-coated glass substrate and dried at 140 °C during 15 min. The blend of polymer (**PGe1-C8**, for example) and [6,6]-phenyl C_{70}-butyric acid methyl ester ($PC_{70}BM$) in chlorobenzene (CB) was spin-coated at different spinning rates. The resulting layers were dried for 24 h in a glovebox and 6 h under reduced pressure before cathode evaporation. The devices were completed by evaporating a lithium fluoride layer followed by the aluminum electrode for an active area of 1 cm^2. The blend of polymer (**PGe1-C8**) and [6,6]-phenyl C_{70}-butyric acid methyl ester ($PC_{70}BM$) and the blend of polymer (**PGe1-EH**) and ($PC_{70}BM$) in chlorobenzene (CB) was spin-coated at different spinning rates. However, the blend of the polymer **PGe2** and $PC_{70}PM$ was deposited at different spinning rates from chlorobenzene (CB) solution containing 3% 1,8-diiodooctane (DIO) as additive. We found for this polymer (**PGe2**) that the device performances can be further improved by changing the devices fabrication solvent from CB to CB containing 3 vol % DIO.

A summary of the photovoltaic performances is reported in Table 2. For polymer **PGe1-C8**, the *J*−*V* curves show a short circuit current (J_{sc}) of 7.8 mA cm^{-2} with an open-circuit voltage (V_{oc}) of 0.53 V and a fill factor (FF) of 0.36. Nevertheless, a PCE of 1.5% was reached for the best cell under an active area of 1 cm^2.

Table 2. Photovoltaic Properties of Polymers **PGe1-C8**, **PGe2**, and **PGe1-EH**

polymer	thickness,[a] nm	J_{sc}, mA cm^{-2}	V_{oc}, V	FF	PCE, %
PGe1-C8	79	7.8	0.53	0.36	1.5
PGe1-EH	75	10.5	0.52	0.53	2.9
PGe2	73	9.7	0.80	0.53	4.1

[a] Thickness of the active layer (polymer:PC$_{70}$BM).

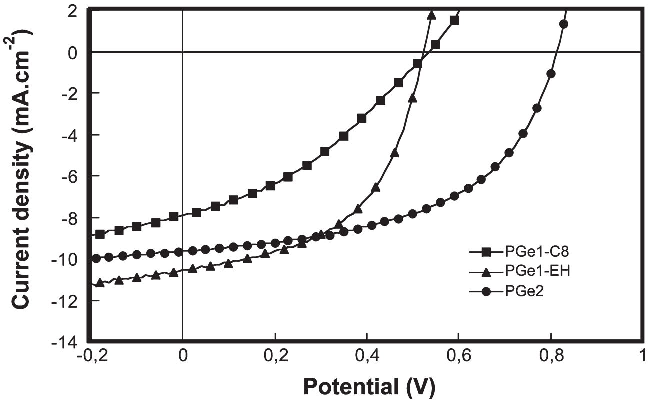


Figure 3. *J*−*V* curves of solar cell based on polymers **PGe1-C8**, **PGe1-EH**, and **PGe2** under illumination of AM 1.5G, 100 mW cm^{-2}.

Then, in the case of **PGe1-EH**, which has 2-ethylhexyl branched side chains, a PCE of 2.9% was obtained. The fill factor (0.53) and the short-circuit current density (10.5 mA cm^{-2}) are higher than **PGe1-C8**. Thus, the open-circuit voltage of **PGe1-EH**, which is related to the energy levels of the polymer, is almost the same as for **PGe1-C8**. If we compare our results with those of Ohshita,[26] who reported a PCE of 1.2% for a similar copolymer, we found that we have obtained a slightly lower V_{oc} but better FF and J_{sc}. The moderate molecular weights of the polymer (**PGe1-C8** and **PGe1-EH**) can also affect solar cell performances. Indeed, Bazan et al.[8] have shown that the molecular weight for this type of system is a key parameter to consider for reaching high power conversion efficiencies in solar cells. At last, a PCE of 4.1% was obtained for polymer **PGe2**. A higher V_{oc} of 0.80 V is obtained with a J_{sc} of 9.7 mA cm^{-2} and a FF of 0.53. This PCE of 4.1% for **PGe2** is clearly not the optimized value and since the dithienogermanium system is still a newcomer to this field. A lot of efforts must be done to further explore its potential in photovoltaic devices. By optimizing parameters such as the molecular weights, processing additives, and annealing, we firmly believe to be able to improve the nanoscale morphology and to enhance the J_{sc}, the V_{oc}, and the PCE of those polymers. Indeed, during the preparation of this paper Reynolds et al. have reported a PCE of 7.3% on devices with the same polymer as **PGe2**.[28] They also observed that devices processed without DIO show low J_{sc}, which can be attributed to the large-scale phase-separated morphology. This clearly supported our claims about the bright future of poly(dithienogermole) derivatives and, in particular, about **PGe2**.

CONCLUSIONS

In summary, we have shown the synthesis of a series of new polydithieno[3,2-*b*:2′,3′-*d*]germole derivatives. The dithieno[3,2-*b*:2′,3′-*d*]germole unit was prepared in few steps with good yields. These polymers possess a good thermal stability and moderate molecular weights. Also, the optical bandgaps of those new polymers are low (1.33−1.67 eV) but comparable with similar polymers materials in the literature. Preliminary results on photovoltaic devices using the **PGe2**:PC$_{70}$BM blend have led to a power conversion efficiency of 4.1% under an active area of 1 cm^2. Finally, to further explore this new class of materials, other units such as 1,4-diketopyrrolopyrroles, quinoxalines, or benzotriazoles should be use to study the effect on the packing, charge transport, and morphology.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, syntheses of the monomers and polymers, instrumentation, and characterization procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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