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ORIGINAL ARTICLE

Synthesis and properties of dithienometallole-pyridinochalcogenadiazole alternate polymers

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Donor–acceptor-type alternate polymers composed of dithienometallole (metal = Si or Ge) and pyridinocalcogenadiazole (chalcogen = S or Se) units with the molecular weights of $M_n = 5700$–7400 ($M_w/M_n = 1.3$–1.7) were obtained as black solids by the Stille coupling reactions of the corresponding bis(trimethylstannyl)dithienometallole and dibromopyridinochalcogenadiazole. Ultraviolet-visible absorption spectra of the polymers showed highly red-shifted broad bands centered at 732–745 nm in chlorobenzene solutions. Bulk heterojunction-type polymer solar cells with blend films of the polymers and $PC_{70}BM$ as the active layers were fabricated, and a maximum power conversion efficiency of 3.46% was obtained using the dithienogermole-pyridinothiadiazole polymer.
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INTRODUCTION

Dithienosilole (DTS) receives a great deal of attention as a building block of functional π-conjugated oligomers[1–3] and polymers.[4,5] In addition to the high planarity of the tricyclic system, bonding interactions between the bithiophene π*- and the silicon σ*-orbital lower the LUMO energy level, leading to efficient conjugation in this system.[6,7] In particular, donor–acceptor-type polymers bearing DTS as the donor have been extensively studied as promising materials of host polymers of bulk heterojunction (BHJ)-type polymer solar cells (PSCs). The interest in these polymers has been particularly strong, since Yang and coworkers[8] prepared a DTS-benzothiadiazole (BTA) alternate polymer (**pDTS-BTA** in Chart 1) and demonstrated its efficient photovoltaic properties—in particular, a high power conversion efficiency (PCE) of 5.1%—as a blend film with $PC_{70}BM$ in the BHJ-type PSC system.

Recent examples of DTS-based photovoltaic donor–acceptor-type polymers include those with dithienylbenzothiadiazole,[9] benzotriazole,[10] phthalimide,[11] thiazolothiazole[12–14] and thienopyrrolodione[15] as the acceptor. Among the PSCs based on these DTS-containing polymers, the DTS-thienopyrrolodione alternate polymer achieved the highest PCE of 7.3%.[15] In 2011, we prepared a dithienogermole (DTG)-BTA alternate polymer (**pDTG-BTA**) as the first example of a DTG-containing photovoltaic polymer (Chart 1) in the hope that replacing the bridging silicon by a heavier germanium atom would enhance the intermolecular interaction, leading to higher carrier-transporting properties of the film.[16] Nearly simultaneously, Reynolds and coworkers[17] reported the synthesis and photovoltaic properties of a DTG-thienopyrrolodione alternate polymer and

demonstrated that the PSC based on this polymer showed better cell performance than that with the analogous DTS-polymer. This enhanced performance was mainly caused by a higher V_{oc} (open-circuit voltage) in the DTG-based alternate polymer. More recently, Leclerc and coworkers[18] reported the high performance of PSCs with similar DTG polymers, among which the highest PCE achieved was 4.1%. We also prepared polymers with an alternate DTG donor and a dithienylbenzothiadiazole or thiazolothiazole acceptor and examined their photovoltaic applications.[19]

In this study, we report the synthesis of alternate polymers composed of a DTS or DTG donor and a pyridinothiadiazole (PTA) or selenadiazole (PSeA) acceptor (Scheme 1), and examined their utility as BHJ-type PSC materials as blends with $PC_{70}BM$ (PTA-DTS-PTA oligomers have been reported, recently. See Henson *et al.*[20]). Pyridinochalcogenadiazole PTA and PSeA with a fused pyridine ring would be more electron-deficient than the benzo-annulated analogues, and thus, a stronger donor–acceptor interaction was anticipated in the present polymers.[20–22] Indeed, both the DTS- and DTG-PTA alternate polymers synthesized in this study showed absorption bands at approximately 740 nm in solution, which were red-shifted from those of **pDTS-BTA** and **pDTG-BTA** with the same substituents on the center metals, as reported previously.[8,10,18]

EXPERIMENTAL PROCEDURE

General

All reactions were carried out in dry argon. Chlorobenzene and ether used as the reaction solvents were distilled from CaH_2 and sodium/benzophenone

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ketyl, respectively, and stored over activated molecular sieves until use. The monomers **DTSSn₂**,[4] **DTGSn₂**[16] and **PTABr₂**[21,22] were prepared as reported in the literature. Nuclear magnetic resonance (NMR) spectra were recorded on Varian 400-MR and System-500 spectrometers (Agilent Inc., Santa Clara, CA, USA). Atmospheric-pressure chemical ionization mass spectra were measured on a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) at N-BARD Hiroshima University, whereas electron impact ionization-gas chromatography (EI-GC) mass spectra were recorded on a Shimadzu QP-2020A spectrometer (Shimadzu Co., Kyoto, Japan). Ultraviolet (UV) absorption spectra were measured on a Hitachi U2910 spectrophotometer (Hitachi High-Tech Co., Tokyo, Japan). Gel permeation chromatography (GPC) was carried out using serially connected Shodex KF2001 and KF2002 columns (Showa Denko K.K., Tokyo, Japan) with tetrahydrofuran as the eluent.

Synthesis of 2,5-dibromopyridinoselenadiazole

A solution of selenium dioxide (0.573 g, 5.162 mmol) in 11 ml of hot water was added slowly to a gently refluxed mixture of 3,4-diamino-2,5-dibromopyridine (1.331 g, 4.987 mmol) and 27 ml of ethanol. The reaction mixture was refluxed for 3 h and cooled to room temperature. The resulting precipitates were collected by filtration and recrystallized from chloroform to provide 1.134 g of 2,5-dibromopyridinoselenadiazole (67% yield) as golden-yellow needles; m.p. > 300 °C; mass spectrometry (MS) m/z 341 (for [79]Br); ^{1}H NMR (δ in CDCl₃, 500 MHz) 8.40 (s, 1H); ^{13}C NMR (δ in CDCl₃, 100 MHz) 158.38, 154.37, 144.21, 139.64, 114.26; Anal. Calcd for C₅HBr₂N₃Se: C, 17.57; H, 0.29; N, 12.29. Found: C, 17.49; H, 0.25; N, 12.25.

Synthesis of dithienometallole-pyridinochalcogenadiazole polymers

A mixture of **DTGSn₂** (0.305 g, 0.387 mmol), **PTABr₂** (0.114 g, 0.387 mmol), Pd₂(dba)₃ (7.1 mg, 0.0080 mmol), P(o-Tol)₃ (11.8 mg, 0.0390 mmol), CuO (30.8 mg 0.387 mmol) and 20 ml of chlorobenzene was placed in a 30-ml two-necked flask. After vacuum degassing, the reaction mixture was heated to reflux for 5 days. The mixture was cooled to room temperature, and the resulting precipitates were filtered. A solution of sodium
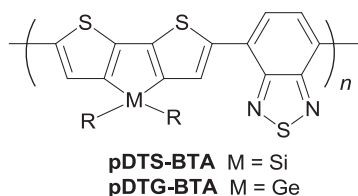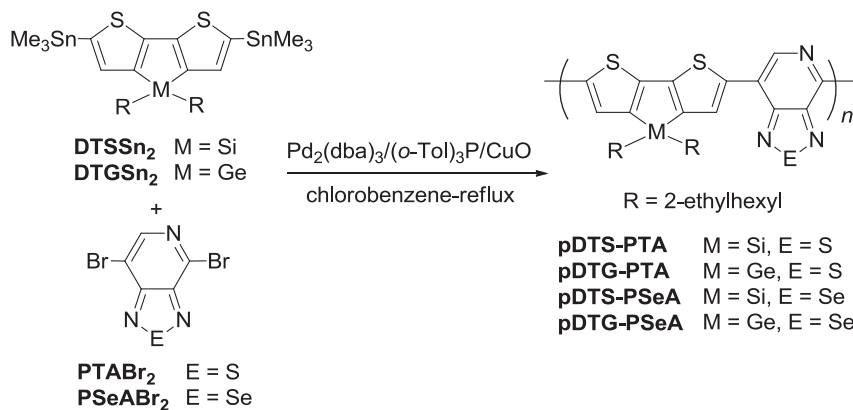
N,N-diethyldithiocarbamate trihydride (3.1 g) in 30 ml of water was added to the filtrate and heated to 80 °C while stirring for 2 h. The organic layer was separated and washed, in order, with water, 3% acetic acid aqueous solution and water again. The organic layer was dried over anhydrous magnesium sulfate, and the solvent was removed under vacuum. Reprecipitation of the residue from chloroform/methanol provided polymeric substances, which were then placed in a Soxhlet apparatus and washed with hot methanol, hexane and ethyl acetate. Finally, the residue, which remained insoluble in these hot solvents, was extracted with hot chloroform. The chloroform solution was then poured into ethyl acetate, and the precipitates were collected and purified by preparative GPC to give **pDTG-PTA** (103.6 mg, 45%) as black solids; m.p. > 300 °C; ^{1}H NMR (δ in CDCl₃, 500 MHz) 8.98-8.80 (m, 1H), 8.80-8.64 (m, 1H), 8.19 (s, 1H), 1.63 (s, 1H), 1.41-1.25 (m, 22H), 0.87-0.84 (m, 12H); ^{13}C NMR (δ in C₆D₅Cl, 125 MHz) 150.05-145.12, 141.39-137.61, 38.79-35.21, 30.17-28.51, 25.67-21.61, 14.48-10.05.

Polymers **pDTS-PTA**, **pDTS-PSeA** and **pDTG-PSeA** were synthesized as black solids through the Stille coupling reaction according to the procedure described above for **pDTG-PTA**. Data for **pDTS-PTA**: 44% yield; m.p. > 300 °C; ^{1}H NMR (δ in CDCl₃, 400 MHz) 8.73-8.45 (m, 2H), 8.17 (s, 1H), 1.63-1.00 (m, 22H), 1.00-0.60 (m, 12H); ^{13}C NMR (δ in C₆D₅Cl, 125 MHz) 36.79-36.17, 30.71-28.38, 24.46-23.10, 16.84-9.31 (aromatic signals may be too broad to be observed). Data for **pDTS-PSeA**: 42% yield; m.p. > 300 °C; ^{1}H NMR (δ in CDCl₃, 500 MHz) 8.75-8.73 (m, 2H), 8.11 (s, 1H), 1.56 (s, 2H), 1.31-1.14 (m, 22H), 0.84 (m, 12H); a weak signal at 8.50 p.p.m. was also observed, most likely due to the terminal bromopyridine units; ^{13}C NMR (δ in C₆D₅Cl, 125 MHz) 36.78-35.41, 30.03-28.51, 23.98-22.41, 19.28-17.60, 14.96-13.29, 11.73-10.61 (aromatic signals may be too broad to be observed). Data for **pDTG-PSeA**: 32% yield; m.p. > 300 °C; ^{1}H NMR (δ in CDCl₃, 400 MHz) 8.74-8.72 (m, 2H), 8.11 (s, 1H), 1.63 (s, 1H), 1.43-1.27 (m, 22H), 0.87-0.86 (m, 12H); a weak signal at 8.49 p.p.m. was also observed, most likely due to the terminal bromopyridine units; ^{13}C NMR (δ in C₆D₅Cl, 125 MHz) 38.38-35.15, 30.13-28.53, 24.03-20.49, 14.89-10.74 (aromatic signals may be too broad to be observed).

Synthesis of 1,1-bis(2-ethylhexyl)-3-bromodithieno[3,2-b:2′,3′-d]germole

A mixture of **DTGBr₂** (4.410 g, 7.100 mmol) and 50 ml of ether was placed in a 100-ml two-necked flask. An *n*-butyllithium solution (4.3 ml, 1.65 M in hexane) was slowly added to this mixture at −80 °C. After stirring this mixture at −80 °C for an additional 30 min, the mixture was hydrolyzed with saturated aqueous NH₄Cl with ice cooling. The organic layer was separated and dried over anhydrous magnesium sulfate. After the solvent was evaporated, the residue was chromatographed on a silica gel column with hexane as an eluent to provide 3.048 g of the title compound as a dark green oil (79% yield); MS m/z 542; ^{1}H NMR (δ in CDCl₃, 400 MHz) 7.22 (d, J = 4.4 Hz, 1H), 7.03 (d, J = 4.4 Hz, 1H), 6.98 (m, 1H), 1.46 (m, 2H), 1.31-1.12 (m, 20H), 0.85-0.77 (m, 12H);

pDTS-BTA M = Si
pDTG-BTA M = Ge

Chart 1 DTS- and DTG-based donor–acceptor-type polymers.

DTSSn₂ M = Si
DTGSn₂ M = Ge

PTABr₂ E = S
PSeABr₂ E = Se

Pd₂(dba)₃/(o-Tol)₃P/CuO
chlorobenzene-reflux

R = 2-ethylhexyl

pDTS-PTA   M = Si, E = S
pDTG-PTA   M = Ge, E = S
pDTS-PSeA M = Si, E = Se
pDTG-PSeA M = Ge, E = Se

Scheme 1 Synthesis of dithienometallole-pyridinochlcogenadiazole polymers.

^{13}C NMR (δ in CDCl$_3$, 400 MHz) 146.86, 145.74, 144.01, 143.92, 143.84, 142.90, 142.79, 142.68, 132.32, 129.67, 125.12, 110.41, 36.91, 35.40, 28.88, 28.65, 22.96, 20.66, 14.10, 10.82; high-resolution MS (atmospheric-pressure chemical ionization) Calcd: [M + H$^+$] 543.08046, Found: 543.08002.

Synthesis of 1,1-bis(2-ethylhexyl)-3-(trimethylstannyl)dithieno[3,2-b:2′,3′-d]germole

A solution of 1,1-bis(2-ethylhexyl)-3-bromodithieno[3,2-b:2′,3′-d]germole (1.289 g, 2.377 mmol) in 15 ml of ether was placed in a 100-ml two-necked flask. An *n*-butyllithium solution (1.45 ml, 1.65 M in hexane) was slowly added to this solution at −80 °C. After stirring at −80 °C for an additional 30 min, trimethyltin chloride (0.513 g, 2.574 mmol) was added, and the mixture was allowed to warm to room temperature. The mixture was poured into ice water, and the organic layer was separated and dried over anhydrous magnesium sulfate. After the solvent was evaporated, the residue was purified by preparative GPC to provide 0.763 g of the title compound as a yellow oil (51% yield); ^{1}H NMR (δ in CDCl$_3$, 500 MHz) 7.17 (d, *J* = 4.5 Hz, 1H), 7.08 (s, 1H), 7.02 (d, *J* = 4.5 Hz, 1H), 1.47 (m, 2H), 1.31-1.16 (m, 20H), 0.84-0.77 (m, 12H), 0.37 (s, 9H); ^{13}C NMR (δ in CDCl$_3$, 125 MHz) 152.06, 146.50, 146.44, 146.38, 145.15, 143.73, 143.58, 143.44, 137.70, 137.35, 129.80, 124.52, 36.98, 36.90, 35.43, 28.93, 28.87, 28.69, 23.00, 20.66, 20.56, 14.14, 10.87, -8.19; high-resolution MS (atmospheric-pressure chemical ionization) Calcd: [M + H$^+$] 629.13474, Found: 629.13507.

Synthesis of 2DTG-PTA

A mixture of 1,1-bis(2-ethylhexyl)-3-(trimethylstannyl)dithieno[3,2-b:2′,3′-d]germole (0.428 g, 0.683 mmol), PTABr$_2$ (0.100 g, 0.339 mmol), Pd$_2$(dba)$_3$ (6.7 mg, 0.007 mmol), (*o*-Tol)$_3$P (11.1 mg, 0.0360 mmol) and 10 ml of chlorobenzene was placed in a 30-ml two-necked flask and heated to reflux for 5 days. The mixture was cooled to room temperature, and the resulting precipitates were filtered. After evaporation of the solvent from the filtrate, the resulting residue was purified by preparative GPC to provide 0.2617 g of 2DTG-PTA (74% yield as a diastereomeric mixture) as a blue oil; ^{1}H NMR (δ in CDCl$_3$, 500 MHz) 8.80 (s, 1H), 8.69 (s, 0.25H), 8.69 (s, 0.5H), 8.68 (s, 0.25H), 8.11 (s, 0.25H), 8.11 (s, 0.5H), 8.10 (s, 0.25H), 7.35 (d, *J* = 4.5 Hz, 1H), 7.29 (d, *J* = 5.0 Hz, 1H), 7.11 (d, *J* = 4.5 Hz, 1H), 7.09 (d, *J* = 4.5 Hz, 1H), 1.53 (m, 4H), 1.37-1.12 (m, 40H), 0.815 (t, *J* = 7.5 Hz, 24H); ^{13}C NMR (δ in CDCl$_3$, 125 MHz) 154.74, 151.483, 148.19, 148.15, 146.49, 146.48, 146.46, 146.43, 146.40, 146.37, 146.34, 146.33, 146.32, 146.31, 146.26, 146.23, 146.19, 145.75, 145.47, 145.43, 145.39, 144.96, 144.86, 144.77, 142.50, 140.34, 137.16, 137.15, 137.14, 134.98, 134.96, 134.94, 130.50, 130.48, 130.47, 130.08, 129.94, 126.99, 125.94, 120.12, 37.02, 36.99, 35.54, 35.51, 35.48, 28.99, 28.96, 28.75, 28.73, 28.68, 23.01, 22.99, 20.84, 20.83, 20.80, 20.78, 20.73, 20.70, 14.14, 14.13, 10.89, 10.84, 10.83; high-resolution MS (atmospheric-pressure chemical ionization) Calcd: [M$^+$] 1061.29826, Found: 1061.29877.

Fabrication and evaluation of PSCs

The polymer photovoltaic devices were fabricated with a typical sandwich structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) poly (styrenesulfonate) (PEDOT:PSS)/DTG polymer: PC$_{70}$BM (85–90 nm)/LiF (0.5 nm)/Al (80 nm). The ITO-coated glass substrates were cleaned with a routine cleaning procedure, including sonication in detergent, distilled water, acetone and 2-propanol, in this order. The ITO surface was further cleaned by exposing it to ozone for 10 min, and a layer of PEDOT:PSS with a thickness of 30 nm was spin-coated onto the cleaned ITO substrate immediately thereafter. The PEDOT:PSS-coated ITO substrate was heated on a hot plate at 150 °C for 10 min. A solution of the polymers: PC$_{70}$BM blend in *o*-dichlorobenzene containing diiodooctane (2.5 vol%) (Diiodooctane is commonly used as an additive to control the film morphology. See Lee *et al.*[23]) was spin-coated onto this heated substrate after filtering through a 0.45 μm poly-tetrafluorethylene syringe filter. The device structure was completed by depositing a LiF (0.5 nm) and Al (80 nm) cathode as the top electrode onto the polymer layer at 10^{-6} torr. The handling of the PEDOT:PSS film after annealing was performed in a glove box equipped with a vacuum deposition apparatus, and the devices were evaluated as follows in an inert atmosphere.

The current density-voltage (*J-V*) characteristics of the PSCs were investigated under illumination with 100 mW cm^{-2} (air mass 1.5 G) simulated solar light from a Peccell PEC-L11 solar simulator (Peccell Technologies, Inc., Kanagawa, Japan). The data were recorded with a Keithley 2400 source-measure unit (Keithley Instruments Inc., Cleveland, OH, USA). The incident photon-to-current conversion efficiency was measured as a function of wavelength from 300 to 900 nm with a halogen lamp as the light source, and calibration was performed with a silicon reference photodiode. The thickness of the thin film was measured with a Veeco Dektak 8 surface profilometer with an accuracy of ± 5 nm.

RESULTS AND DISCUSSION

Polymer synthesis

Stille coupling reactions of bis(trimethylstannyl)dithienometallole (DTSSn$_2$ and DTGSn$_2$) with dibromopyridinochalcogenadiazole (PTABr$_2$ and PSeABr$_2$) using Pd$_2$(dba)$_3$/(*o*-Tol)$_3$P/CuO as the catalyst, followed by the purification of the resulting organic products by Soxhlet extraction, yielded the corresponding polymers as black solids that were soluble in hot chloroform but insoluble in hot methanol, hexane and ethyl acetate (Scheme 1). At ambient temperature, these purified polymers showed good solubility in chloro- and *o*-dichlorobenzene and moderate solubility in chloroform and tetrahydrofuran, but were insoluble in toluene and ethanol. Table 1 summarizes the properties of these polymers. Molecular weights, determined by GPC relative to polystyrene standards, were M_n = 5700–6200 with polydispersity (M_w/M_n) of 1.3–1.7. The lower

Table 1 Synthesis and properties of dithienometallole-pyridinochlcogenadiazole polymers

Polymer	Method[a]	Yield (%)	M_n (M_w/M_n)[b]	TGA ($T_d^5/°C$)[c]	UV-vis ($λ_{max}$/nm)		HOMO (eV)[d]	LUMO (eV)[e]
					PhCl	Cast film		
pDTS-PTA	A	29	5800 (1.3)	420	732	742	−5.11	−3.67
pDTS-PTA′	B	44	7400 (1.7)	—[f]	726[g]	—[f]	—[f]	—[f]
pDTG-PTA	A	45	6200 (1.5)	405	745	739	−5.03	−3.67
pDTG-PTA′	B	40	6300 (1.5)	—[f]	734[g]	—[f]	—[f]	—[f]
pDTS-PSeA	A	42	5700 (1.5)	342	740	805	−5.22	−3.97
pDTG-PSeA	A	32	5700 (1.5)	377	741	778	−5.03	−3.78

Abbreviations: TGA, thermogravimetric analysis; UV-vis, ultraviolet-visible.
[a]Polymerization method. With CuO as cocatalyst (A) and without CuO (B).
[b]Determined by GPC, relative to polystyrene standards.
[c]In nitrogen at 10 °C min^{-1}.
[d]Based on cyclic voltammogram oxidation peak onset of polymer cast film.
[e]Calculated by HOMO level and optical band gap.
[f]Not measured.
[g]In chloroform.

molecular weights of the present polymers relative to those of **pDTS-**[8] and **pDTG-BTA**[16,18] were ascribed to the lower solubility properties of the present polymers. Polymeric substances with high molecular weights were likely removed as solids that were insoluble in hot chloroform.

The polymer structures were verified mainly by ^{1}H NMR spectroscopic analysis. Although the spectra showed only broad signals, the integration ratios of the ^{1}H NMR spectra were nearly consistent with the regular alternate structure shown in Scheme 1, with a random orientation of the pyridine nitrogen atom. In the spectra of **pDTS-**
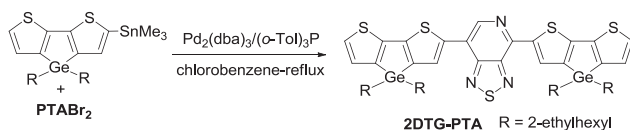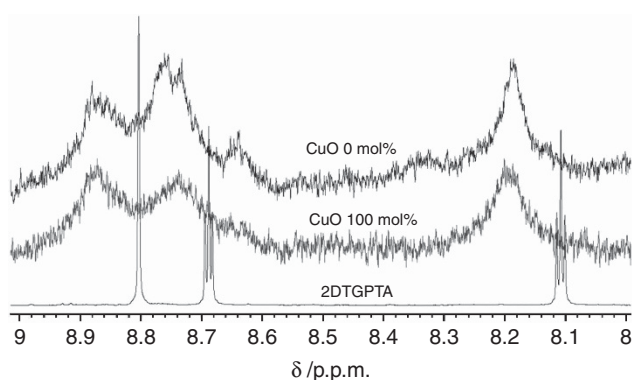
Scheme 2 Synthesis of model compound.

Figure 1 Aromatic regions of the ^{1}H NMR spectra of **pDTG-PTA**′ (top), **pDTG-PTA** (middle) and **2DTG-PTA** (bottom) in CDCl$_3$. Signal splitting at approximately 8.1 and 8.7 p.p.m. for **2DTG-PTA** is ascribed to the existence of diastereomeric germylene units, with respect to two chiral 2-ethylhexyl substituents.

and **pDTG-PSeA**, however, the unidentified weak CH signals were also observed, most likely due to the terminal bromopyridine units. The ^{1}H NMR spectrum of **pDTG-PTA** resembled that of a model compound (**2DTG-PTA**), which was prepared in a 74% isolated yield by Stille coupling under similar conditions to those of the preparation of **pDTG-PTA** (Scheme 2 and Figure 1).

The UV-visible absorption spectra of the polymers were measured in the solution and film states, as depicted in Figure 2. These spectra showed broad absorption bands with maxima at approximately 730 nm in chlorobenzene, and thus, were largely red-shifted from the absorption bands of **2DTG-PTA** (λ_{max} = 584 nm). The absorption bands were not significantly affected by the metal type (M = Si or Ge) or the chalcogen atom type (E = S or Se), but the bands were again markedly red-shifted from those of **pDTS-** and **pDTG-BTA** reported previously (λ_{max} = 670 nm for DTS,[8] 651 nm[16] and 691 nm[18] for DTG polymers, respectively). This red-shifting is presumably due to the higher electron-deficiency properties of PTA and PSeA relative to the properties of BTA and also the increased planarity of the pyridine polymers resulting from the replacement of the benzene ring with a sterically less repulsive pyridine ring.

All the present polymers exhibited even broader absorption bands when the spectra were measured on their cast films. For **pDTS-** and **pDTG-PSeA**, the absorption maxima of the films were red-shifted from those in solution, indicating the intermolecular interaction of the polymers in the solid states. In contrast, **pDTS-** and **pDTG-PTA** showed no remarkable changes of the λ_{max} values between the measurement states (solution or film). However, a clear enhancement of the shoulder peaks at about 850 nm was observed for these PTA-polymer films, again indicating the facilitated intermolecular interaction of the polymers in the solid states. The electronic states of the polymer cast films were further investigated by cyclic voltammograms. The films revealed oxidation peak onsets at approximately 0.3 V vs Fc/Fc$^+$, corresponding to HOMO levels of (-5.2) to (-5.0) eV (Table 1), at nearly the same potential as those of **pDTS-BTA** (-5.05 eV)[8] and **pDTG-BTA** (-5.00 eV),[16] indicating that the decrease of the LUMO is responsible for the red-shifted
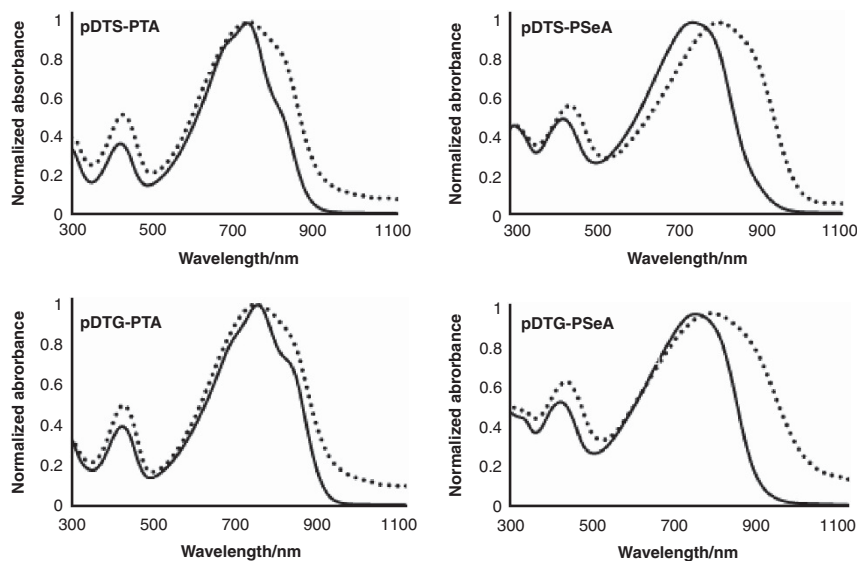
Figure 2 UV spectra of dithienometallole-pyridinochalcogenadiazole polymers in chlorobenzene (solid line) and as films (dotted line).
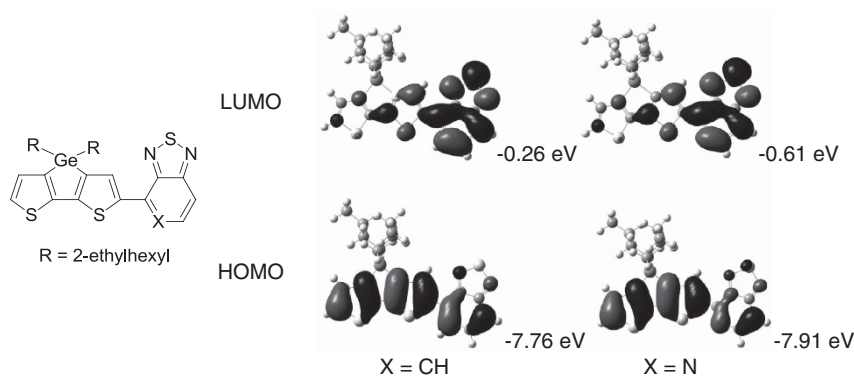
Figure 3 Molecular structures, and energy levels and profiles of HOMOs and LUMOs of model compounds DTG-BTA (left) and -PTA (right), derived from density functional theory calculations at LC-BLYP/6–31G(d,p).

absorption of the present PTA- and PSeA-containing polymers, relative to the BTA analogues.

We also examined the Stille coupling of **DTSSn₂** and **DTGSn₂** with **PTABr₂**, using the Pd₂(dba)₃/(o-Tol)₃P catalyst without CuO (polymers **pDTS-** and **pDTG-PTA′**). The resulting polymers showed NMR profiles that were similar to, but slightly different from, those prepared in the presence of CuO (**pDTS-** and **pDTG-PTA**). For example, **pDTG-PTA′** exhibited small ^{1}H NMR signals at approximately 8.33 and 8.64 p.p.m. in the aromatic proton region, signals that were not clearly observed in the spectrum of **pDTG-PTA** (Figure 1). Furthermore, the UV absorption bands moved to slightly higher energies from those of **pDTS-** and **pDTG-PTA** (Table 1). These results are to some extent indicative of the structural irregularity in **pDTS-** and **pDTG-PTA′**, although we have no further evidence to characterize the detailed polymer structures.

To understand how the pyridine ring affected the polymer electronic states, we carried out density functional theory calculations on models of **DTG-PTA** and -**BTA** at the level of LC-BLYP/6-31G(d,p).[24] The HOMO and LUMO profiles and the energy levels derived from the calculations are presented in Figure 3, showing that the HOMO of these model compounds is rather localized on the DTG segment, whereas the LUMO mostly lies on the BTA/PTA unit, suggesting their charge-separated photo-excited states. Both the HOMO and the LUMO are stabilized upon replacing the BTA unit by PTA, as we expected. However, the decrease of the LUMO is larger than that of the HOMO. This difference in the magnitude of the decrease between the LUMO and the HOMO is primarily responsible for the reduced HOMO-LUMO energy gap of **pDTG-PTA** compared with that of **pDTG-BTA**, in accordance with the polymer optical and electrochemical properties (*vide infra*).

We also performed a thermogravimetric analysis of the present polymers in nitrogen, illustrating their good thermal stability (Table 1). Higher T_d^5 (temperature of 5% weight loss) was noted for the PTA-polymers than for the PSeA analogues. The TG profile of **pDTG-PTA** resembled that reported for **pDTG-BTA**.[18] No unambiguous signals were observed in the differential scanning calorimetry measurements of the present polymers.

PSC fabrication and evaluation

BHJ-type PSCs using the present polymers as the host materials were fabricated with the structure of ITO (150 nm)/PEDOT:PSS (30 nm)/ dithienometallole-pyridinochlogenadiazole polymer: PC₇₀BM (85– 90 nm)/LiF (0.5 nm)/Al (80 nm) and an active area of 0.25 cm². The
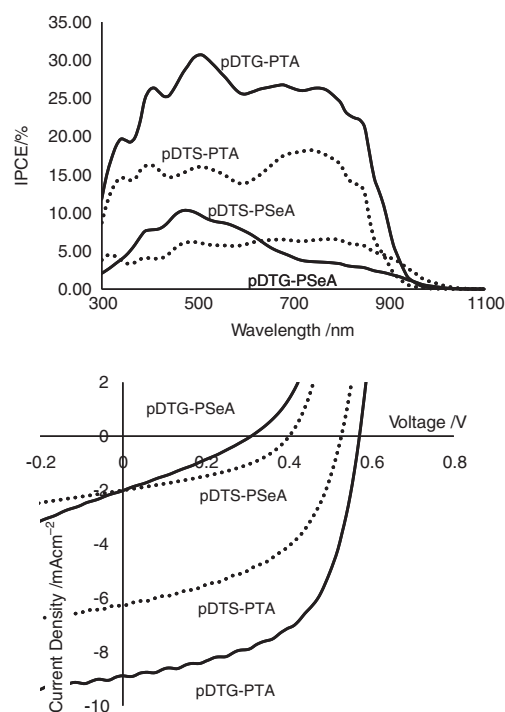

Figure 4 Incident photon-to-current conversion efficiency (IPCE) spectra (top) and current density-voltage (*J-V*) characteristics (bottom) of PSCs based on DTG (solid line) and DTS (dotted line)-pyridinochalcogenadiazole polymers.

active layers were prepared by spin-coating 46 mg ml⁻¹ *o*-dichlorobenzene solutions of the polymer:PC₇₀BM blends in a weight ratio of 1:3.6 containing 2.5 vol% of diiodooctane. Annealing of the active layers as well as the devices did not affect the results. As expected, the cells showed clear photovoltaic properties whose incident photon-to-current conversion efficiency (IPCE) spectra and current density-voltage (*J-V*) curves are depicted in Figure 4.

The cell parameters are summarized in Table 2. The cells with PSeA polymers showed much lower performance than those with PTA polymers. Although their IPCE spectra did not fit the UV spectra of the polymer films well (Figure 2), the spectral edges reached to approximately 960 nm, reflecting the low-band gap properties of the PSeA polymers. The best performance among these PSCs was achieved by employing **pDTG-PTA** with the PCE = 2.92%. With **pDTG-PTA**, we optimized the solution concentration of the

Table 2 Performance of PCSs based on dithienometallole-pyridinochalcogenadiazole[a]

Polymers.polymer	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
pDTS-PTA	0.53	6.29	0.49	1.65
pDTS-PTA'	0.53	5.64	0.45	1.36
pDTG-PTA	0.57	8.89	0.57	2.92
pDTG-PTA'	0.54	7.54	0.52	2.13
pDTS-PSeA	0.40	2.01	0.41	0.33
pDTG-PSeA	0.31	2.02	0.29	0.18

Abbreviations: FF, fill factor; PCE, power conversion efficiency; PCS, polymer solar cell.
[a]ITO (150 nm)/PEDOT:PSS (30 nm)/dithienometallole-pyridinochlcogenadiazole
polymer:PC$_{70}$BM = 1: 3.6 (ca. 100 nm)/LiF (0.5 nm)/Al (80 nm).

blend material for spin coating and the polymer/PC$_{70}$BM ratio (60 mg ml^{-1}, polymer:PC$_{70}$BM = 1:2.5) to improve the PCE up to 3.46% with V_{oc} = 0.54 V, J_{sc} = 12.64 mAcm^{-2} and fill factor = 0.51. The PSCs with polymers **pDTS-PTA'** and **pDTG-PTA'** that were prepared in the absence of CuO gave rise to inferior performance when compared with the PSCs with **pDTS-PTA** and **pDTG-PTA**, respectively, likely due to the less-expanded conjugation, as evidenced by their blue-shifted absorption maxima.

CONCLUSIONS

We synthesized new low-band gap polymers composed of repeating dithienometallole and pyridinochalcogenadiazole units. The dithienometallole-pyridinothiadiazole polymers exhibited highly red-shifted absorption maxima from those of the BTA analogues, in accordance with the results of the density functional theory calculations on the polymer models at LC-BLYP/6-31G(d,p). We fabricated BHJ-type PSCs using the present polymers as the host materials and PC$_{70}$BM as the dopant and obtained the maximum PCE of 3.46% based on the **pDTG-PTA** polymer, which was higher than those reported for similar devices based on **pDTG-BTA**,[16,18] but lower than the **pDTS-BTA**-based device.[8] This result is likely due to the low molecular weights of the present polymers, which affect the film morphology, polymer stacking and absorption properties. Indeed, the performance of the BHJ-type cells based on **pDTS-BTA** was markedly improved by increasing the molecular weight, that is, PCE = 0.71% with V_{oc} = 0.58 V, J_{sc} = 2.43 mA cm^{-2} and fill factor = 0.51 for M_n = 8000, and PCE = 1.21% with V_{oc} = 0.61 V, J_{sc} = 4.68 mA cm^{-2} and fill factor = 0.43 for M_n = 15 000.[16] Further optimization of the polymer structure is under way.

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