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Citation	Polymer , 52 (18) : 3912 - 3916
Issue Date	2011
DOI	10.1016/j.polymer.2011.07.009
Self DOI	
URL	https://ir.lib.hiroshima-u.ac.jp/00034817
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Relation	

Synthesis, characterization, and photovoltaic applications of dithienogermole-dithienylbenzothiadiazole and -dithienylthiazolothiazole copolymers

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Abstract

New dithienogermole-based conjugated polymers were synthesized by the Stille coupling reactions of distannyldithienogermole and dibromoarene, and their photovoltaic properties were studied. These polymers possess low band gaps with broad absorptions covering the 400-800 nm range, and exhibit good film forming properties. Bulk hetero-junction solar cells prepared from blends of these polymers with $PC_{70}BM$ exhibit high power conversion efficiency up to 2.38%.

Keywords: Germole; Polymer solar cell; Bulk hetero-junction

1. Introduction

Polymer solar cells (PSCs) are of current interest due to their potential applications to low cost, lightweight, and flexible modules. Easy manufacturing by the solution process is also

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an advantage of PSCs [1, 2]. Much attention has been focused on bulk hetero-junction (BHJ)-type devices whose active layer is composed of a mixture of an electron-donating conjugated compound and an electron-accepting fullerene derivative, such as PCBM [3,4]. To date, a variety of π-conjugated donor-acceptor (D-A)-type polymers with low band gaps and low-lying HOMOs have been designed and investigated as donor materials for PSCs, as those polymers can absorb solar light of a wide wavelength range and provide high open-circuit voltage (V_{oc}) [2, 5, 6]. Dithienosilole (DTS), silicon-bridged bithiopehene, has been studied as a unique π-conjugated system with low-lying HOMO and LUMO [7, 8] and often employed as the donor component of D-A-type polymers for PSCs [8-17]. It was recently demonstrated that use of a DTS-benzothiadiazole alternating polymer (**DTS-BTA**) leads to high-performance PSCs with high power conversion efficiency (PCE) of 5.1% compared to its carbon analogue (**DTC-BTA**) [9] (Chart 1). This is due to not only the unique electronic states of DTS, but also the capability of the DTS polymer to form higher crystallinity films when blended with PCBM. Similarly, dithienocyclopentadiene-based polymer **DTC-Tz** was modified by replacing the ring carbon with a silicon atom (**DTS-Tz**) to improve the PCE of the PSCs from 2.7% to 4.7% [17].

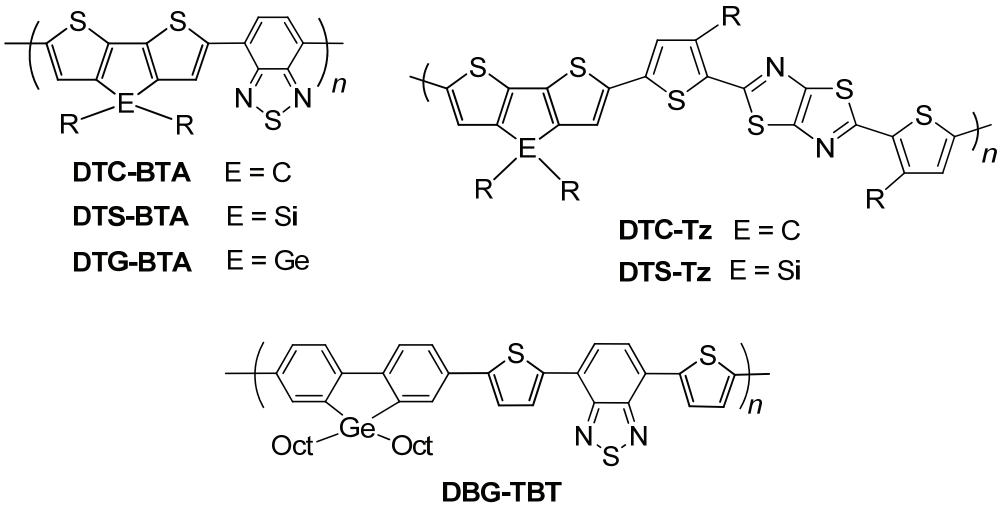


Chart 1. Dithienometallole- and dibenzogermole-based polymers.

Recently, we prepared the first dithienogermole-containing D-A-type polymer (**DTG-BTA**) (Chart 1), that features repeating units of dithienogermole and benzothiadiazole in hopes that the replacement of the silicon with a heavier germanium atom would lead to better intermolecular interaction in the solid state and thus higher crystallinity. As expected, the polymer showed broad absorption spectra with an absorption edge at approximately 850 nm and was used in the manufacture of BHJ-type PSC by blending with $PC_{70}BM$ [18]. Although the PSC showed a clear photovoltaic response, PCE was 1.2%, which was lower than that of **DTS-BTA**, and this was primarily ascribed to the low J_{sc} of the PSC with **DTG-BTA**. A similar dibenzogermole-based polymer **DBG-TBT** was prepared by Leclerc and coworkers, and the blend film of **DBG-TBT** with $PC_{70}BM$ showed photovoltaic application with PCE of 2.8% (Chart 1) [19].

To develop DTG-based host polymers for PSCs that would improve the performance of PSCs, dithienylbenzothiadiazole and dithienylthiazolothiazole moieties were introduced into the backbone as acceptor units and their photovoltaic properties were investigated when blended with $PC_{70}BM$. The more expanded conjugation of the acceptor unit TBT than BTA is expected to enhance polymer interchain interaction in the solid state, thus increasing current density.

2. Experimental

2.1. Materials

All reactions were carried out in dry nitrogen or argon. Tetrahydrofuran (THF) and ether were distilled from sodium/benzophenone, whereas chlorobenzene was distilled from calcium hydride. These solvents were stored over activated molecular sieves until use. Monomers, **DTGSn$_2$** [18], 3,6-bis(5-bromo-2-thienyl)benzo[3.4]thiaziazole [20], and 2,5-bis(5-bromo-4-hexyl-2-thiophenyl)thiazolo[5,4-d]thiazole [21] were prepared according to the method in the literature.

2.2. Characterization

NMR spectra were recorded on a JEOL model LA-400 spectrometer. UV-Vis spectra were measured with a Hitachi U-2910 spectrometer. Polymer molecular weights were measured by gel permeation chromatography (GPC) using Shodex KF804 and KF806 columns connected in series and eluted with THF. The polymers were detected by a UV detector at 240 nm and the molecular weights were calculated relative to the polystyrene standards on a SIC-480 data station. TGA was carried out on a SIC model TG/DTA-6200 in nitrogen at a rate of 10^{o}C/min. Cyclic voltammetry (CV) was performed using VersaSTAT3. Each sample (1-2 mg) was homogeneously dissolved into a 0.2 mL of 10 mM tetrabutylammonium perchlorate (TBAP)/dichloromethane solution, and the solution was cast on a Pt disc electrode (3 mm diameter) and dried in vacuum (< 0.1 Torr) prior to the measurement, as the working electrode. Measurement was performed at a scan rate of 10 mV/s at room temperature with a Pt plate as the counter electrode and an Ag/Ag^{+} reference electrode, in acetonitrile containing 0.1 M TBAP.

2.3. PSC fabrication and evaluation

The polymer photovoltaic devices were fabricated with a typical sandwich structure of ITO/PEDOT:PSS/DTG-polymer:$PC_{70}BM$ (80 nm)/LiF (0.5 nm)/Al (80 nm). The ITO-coated glass substrates were cleaned with a routine cleaning procedure, including sonication in detergent followed by distilled water, acetone, and 2-propanol. A 30 nm thick layer of PEDOT:PSS was spin-coated on the cleaned ITO substrate, after exposing the ITO surface to ozone for 10 min. The PEDOT:PSS-coated ITO substrate was heated on a hot plate at 150^{o}C for 10 min. The DTG-polymers:$PC_{70}BM$ solution in *o*-dichlorobenzene with diiodooctane (2.5 vol%) was spin-coated after filtering through a 0.45 μm PTFE syringe filter. The device structure was completed by depositing LiF (0.5 nm) and Al (80 nm) cathode as the top electrode onto the polymer layer under 10^{-6} torr vacuum in a thermal evaporator. Current density-voltage (*J-V*) characteristics of all PSCs were measured under illumination with 100 mW/cm^2 (AM 1.5G) simulated solar light from a Peccell PEC-L11 solar simulator. Data were recorded with a Keithley 2400 source-measure unit and all characterizations were

carried out in an ambient environment. Incident photon-to-current conversion efficiency (IPCE) 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. Thickness of the thin film was measured with a Veeco Dektak 8 surface profilometer with an accuracy of ± 5 nm.

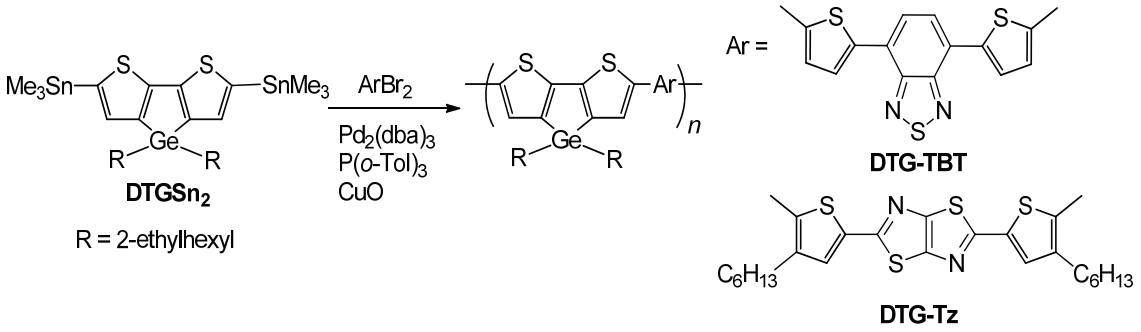
2.4. Polymer synthesis

In 7 mL of chlorobenzene were dissolved 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (0.160 g, 0.353 mmol) and bis(2-ethylhexyl)bis(trimethylstannyl)dithienogermole (**DTGSn$_2$**, 0.279 g, 0.353 mmol). The mixture was purged with a gentle stream of argon for 10 min, and tris(dibenzylideneacetone)dipalladium(0) (8 mg, 2 mol%), tri(*o*-tolyl)phosphine (18.7 mg, 16 mol%), and CuO (29.6 mg, 0.353 mmol) were added. The resulting mixture was heated at 150 °C for 72 h and cooled to room temperature. To this was added 100 mL of methanol to precipitate polymeric substances. The polymeric substances were washed with hot methanol and then with hot hexane in a Soxhlet apparatus. Finally the methanol- and hexane-insoluble substances were extracted with hot chloroform. Evaporation of the solvent from the extract, followed by drying the residue under vacuum for 1 day at room temperature gave **DTG-TBT** as a black solid (100 mg, 50 % yield, M_n = 3.8 K, PDI = 3.15): ^{1}H NMR (ppm, $CDCl_3$) δ = 8.30-6.32 (br, 8H), 1.53-1.43 (br, 4H), 1.41-1.05 (m, 20H), 0.93-0.72 (m, 10H), mp: 180°C. Polymer **DTG-Tz** was prepared in a manner similar to that above. Data for **DTG-Tz**: dark green solids. 75% yield. M_n = 11 K, PDI = 2.34). ^{1}H NMR (ppm, $CDCl_3$) δ = 7.41 (br, 2H), 7.2 (br, 2H), 2.8 (br, 4H), 1.72 (br, 6H), 1.50-1.06 (m, 30H), 1.05-0.66 (m, 20H), mp: 240 °C.

3. Results and discussion

The DTG-polymers were prepared under the conditions that were optimized for the preparation of **DTG-BTA**, utilizing the CuO-modified Stille coupling reactions [22] of **DTGSn$_2$** with bis(bromothienyl)benzothiadiazole and bis(bromohexylthiophene)thiazolo-

thiazole at 150°C (Scheme 1). The organic products were fractionated with a Soxhlet apparatus to give polymers **DTG-TBT** and **DTG-Tz** as black and dark green solids, respectively, which are soluble in hot chloroform, but insoluble in hot methanol and hexane. The number-average molecular weights (M_n) of the polymers were determined by GPC using polystyrene standards to be 3.8 K (PDI = 3.2) for **DTG-TBT** and 11 K (PDI = 2.3) for **DTG-Tz**. The polymer structures were verified mainly from the ^{1}H NMR spectra (Figure 1). Although the spectra showed only broad signals, the signal integration ratios almost agreed with those of the regularly alternating structures of DTG and benzothiadiazole or thiazolothiazole units shown in Scheme 1. A similar reaction of **DTGSn$_2$** and bis(bromothienyl)benzothiadiazole in the absence of CuO also gave a polymeric substance. However, its ^{1}H NMR spectrum showed very broad and unresolved aromatic proton signals with much less integration than expected. Attempted improvement of the molecular weights and the product yields under forcing conditions, at 170°C in an autoclave, did not affect the results for **DTG-Tz**. Thermal properties of the polymers were evaluated by TGA under a nitrogen atmosphere and **DTG-TBT** and **DTG-Tz** were found to show good stability with 5 % weight loss temperatures of 382°C and 340°C, respectively. The molecular weights and thermal properties of the polymers are summarized in Table 1.



Scheme 1. Synthesis of DTG-based polymers.

The UV-vis absorption spectra of the present DTG-based polymers in chloroform and as solid thin films prepared by spin-coating are shown in Figure 2a and the absorption wavelengths are listed in Table 1. In chloroform, **DTG-TBT** shows an absorption

maximum at 585 nm, which appears at a higher energy than that of **DTS-TBT** (ca. 630 nm) as reported in the literature [12]. In film, the absorption band shifts to a longer wavelength (λ_{max} = 620 nm). Although this still appears at a higher energy than that of **DTS-TBT** in film (650 nm), the difference in absorption maxima of **DTG-TBT** depending on the conditions, $\Delta\lambda_{max}$ = (λ_{max} in film – λ_{max} in chloroform) = 35 nm, is larger than that of **DTS-TBT** ($\Delta\lambda_{max}$ = 20 nm), indicating the strong interchain interaction of **DTG-TBT** in the solid state. As reported previously, the UV spectra of **DTG-BTA** always showed broad absorption maxima at 651 nm and 687 nm in chloroform and as film, respectively, and the absorption maxima were longer than those of the present **DTG-TBT** [18]. The introduction of a thienylene unit into the DTG-benzothiadiazole bond is likely to reduce the D-A interaction between them. A similar tendency was observed for **DTS-BTA** [8] and **DTS-TBT** [12].

Similar to **DTG-TBT**, **DTG-Tz** shows a large shift of the absorption maximum from 542 nm in chloroform to 589 nm in film ($\Delta\lambda_{max}$ = 47 nm). In addition, a shoulder around 650 nm appears for **DTG-Tz** in film, again indicating the strong interchain interaction. The optical band gaps of the DTG-based polymers were estimated from the absorption edges in the UV-vis spectra of the films to be 1.60 and 1.80 eV for **DTG-TBT** and **DTG-Tz,** respectively (Table 1). They are very similar to those reported for **DTS-TBT** (1.51-1.53 eV) [12] and **DTS-Tz** (1.83 eV) [17]. The CV measurements were carried out for the DTG-polymer films on Pt wires at the rate of 10 mV/sec (Figure 3). The HOMO energy levels of **DTG-TBT** and **DTG-Tz** were calculated to be both -5.05 eV, based on the CV oxidation onsets (E_{HOMO}/eV = –4.8 – [E_{onset}–$E_{1/2}$ (Ferrocene)]/V), and the LUMO energy levels were calculated to be –3.45 eV (**DTG-TBT**) and –3.25 eV (**DTG-Tz**) from the optical band gaps and the electrochemical HOMO energy levels. They are in good relationship with the electronic states of PEDOT-PSS and $PC_{70}BM$ (Figure 2b [23]), to facilitate efficient charge separation and hole transfer to PEDOT-PSS.

PSCs were fabricated with the structure of ITO/PEDOT:PSS/DTG-polymers:$PC_{70}BM$ (1:3.6) /LiF [24] /Al and the active area of 0.25 cm^2. Diiodooctane, which is often used as a

processing additive to control phase separation, was added for the spin-coating of the blend films [25]. In fact, when diiodooctane was not used, the power conversion efficiency (PCE) of the **DTG-BTA**-based cell [18] dropped to approximately a half of that prepared using iiodooctane. No annealing was applied. The typical *J-V* characteristics and the IPCE plots of the devices are depicted in Figure 4. As summarized in Table 2, the **DTG-TBT**-based cell exhibits the performance parameters of J_{sc} = 5.47 mA/cm^2, V_{oc} = 0.59 V, and FF = 0.48, giving rise to PCE of 1.55 %. Under the same conditions, higher cell parameters are obtained from the **DTG-Tz**-based PSC (J_{sc} = 6.31 mA/cm^2, V_{oc} = 0.58 V, FF = 0.65, and PCE = 2.38 %), mainly arising from the higher FF of the PSC fabricated with **DTG-Tz** than that with **DTG-TBT** (Table 2 and Figure 4a), which usually means better phase separation and more efficient charge dissociation in the films. The present PSCs show improved photovoltaic performance, compared with PSCs fabricated with **DTG-BTA**, reported previously (PCE = 1.2%, Table 2) [18], in spite of that **DTG-BTA** shows more extended conjugation as evidenced by the longer λ_{max} (651 nm in chloroform and 687 nm in film). This is probably due to the enhanced interchain interaction in **DTG-TBT** and **DTG-Tz**. The IPCE of the PSCs start to increases around 730 nm and 810 nm, and reach 27 % at 460 nm and 35 % at 600 nm for **DTG-TBT** and **DTG-Tz**, respectively as shown in Figure 4b. The PCEs of similar PSCs with **DTS-TBT** and **DTS-Tz** were reported to be higher (3.43% and 4.7%) than those of the present PSCs, due to the higher current density (10.67 and 11.8 mA/cm^2) for the DTS-based PSCs [12, 17].

4. Conclusions

We have designed and synthesized new DTG-based low-band gap polymers composed of relatively electron-rich DTG units and electron-deficient benzothiadiazole or thiazolothiazole units in the backbone. **DTG-TBT** and **DTG-Tz** polymers show broad absorptions covering 300 nm to 700-800 nm with the optical band gaps of 1.60 and 1.80 eV for **DTG-TBT** and **DTG-Tz**, respectively. They feature good thermal stability and good solubility in common organic solvents as well as high photovoltaic performance when blended with $PC_{70}BM$,

compared with the previously reported DTG-benzothiadiazole polymer (**DTG-BTA**). However, the PCEs are still lower than those of PSCs fabricated with the DTS analogues, due to the lower current density. Current density may be improved by increasing polymer molecular weights. Optimization of the polymer structures by tuning the substituents may also influence polymer packing structures in films, thereby improving the current density. Further studies to improve the performance of the present DTG-based PSCs are under way.

Acknowledgement. This work was supported in part by a Grant–in–Aid for Scientific Research (No.23350097) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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Table 1

Synthesis and properties of DTG-containing polymers.

Polymer	Yield/%	M_n[b]	PDI[b]	T_d/°C[c]	UV-vis λ_{max}/nm		Eg/eV[d]
					In $CHCl_3$	Film	
DTG-TBT[a]	50	3,800	3.15	382	585	620	1.60
DTG-Tz[a]	75	11,000	2.34	340	542	589	1.80

[a] Polymeric substance that is soluble in hot chloroform but insoluble in hot methanol and hexane was collected.

[b] Determined by GPC, relative to polystyrene standards.

[c] Decomposition temperature (with 5% weight loss) determined by TGA under N_2.

[d] Optical band gap calculated from the absorption onset in film.

Table 2

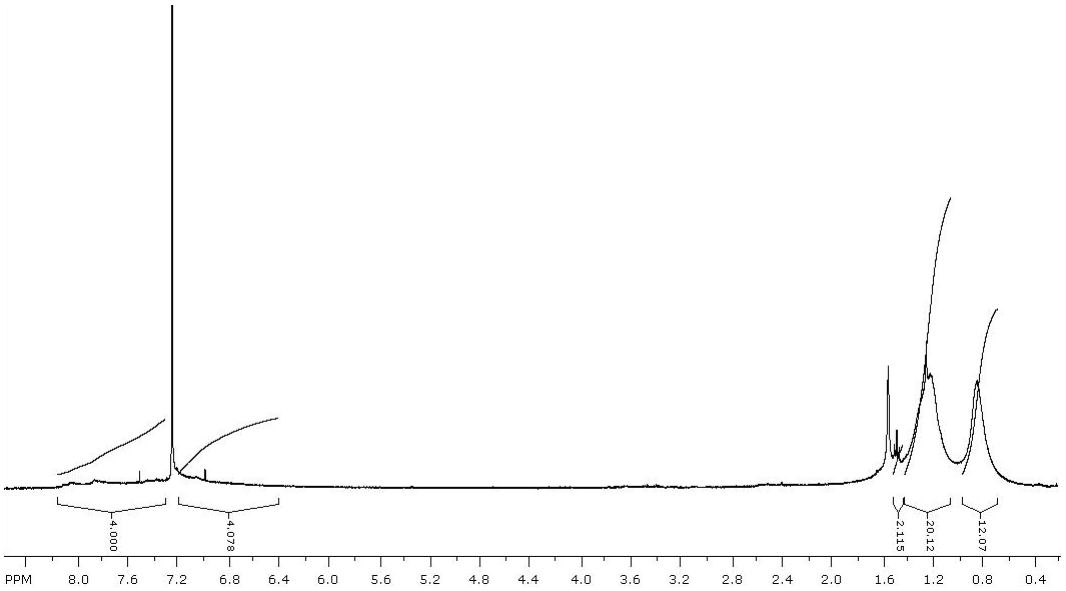
Performance of PSCs based on DTG-containing polymers as host materials.[a]

Polymer	J_{sc}/mAcm^{-2}	V_{oc}/V	FF	PCE/%
DTG-TBT	5.47	0.59	0.48	1.55
DTG-Tz	6.31	0.58	0.65	2.38
DTG-BTA[b]	4.68	0.61	0.43	1.21

[a] PSCs structure: ITO (150 nm)/PEDOT:PSS (30 nm)/DTG-polymer:$PC_{70}BM$ (1:3.6 wt%, 80 nm)/LiF (0.5 nm)/Al (80 nm).

[b] See reference 18.

a)



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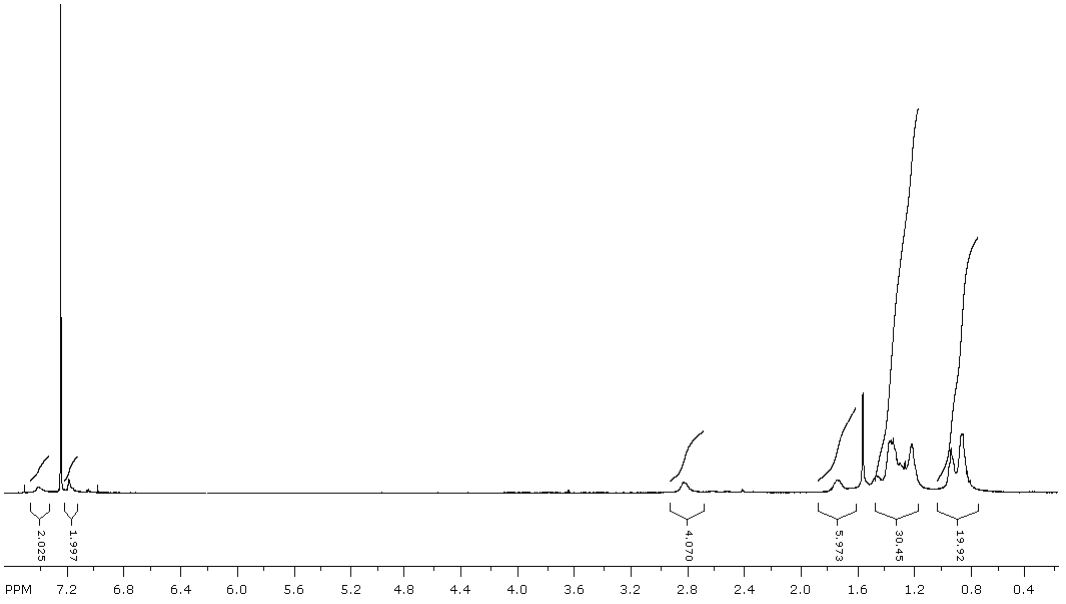
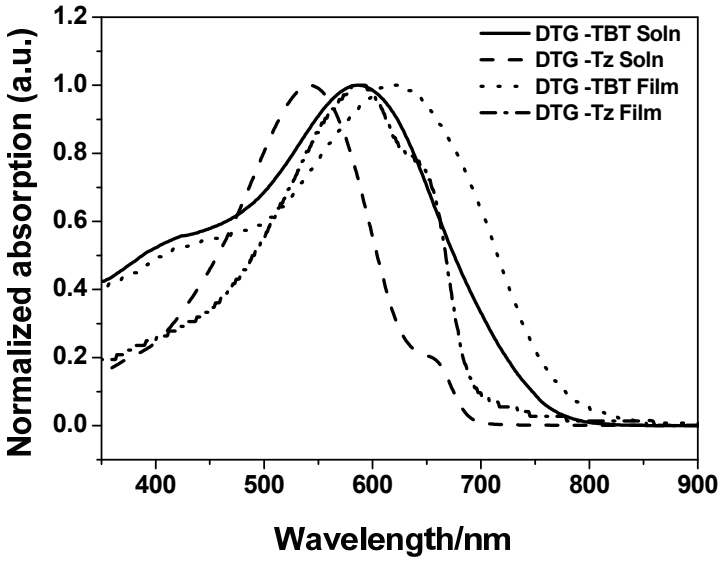


Figure 1. ^{1}H NMR spectra of a) **DTG-TBT** and b) **DTG-Tz** in $CDCl_3$.

a)



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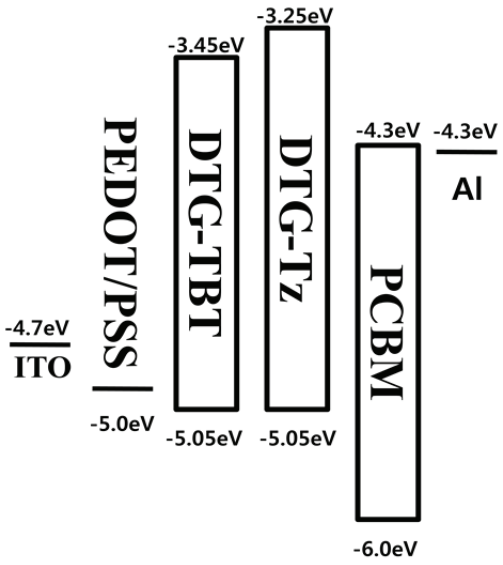


Figure 2. a) UV-vis absorption spectra of DTG-containing polymers in chloroform and as films. b) Energy levels for the polymers.

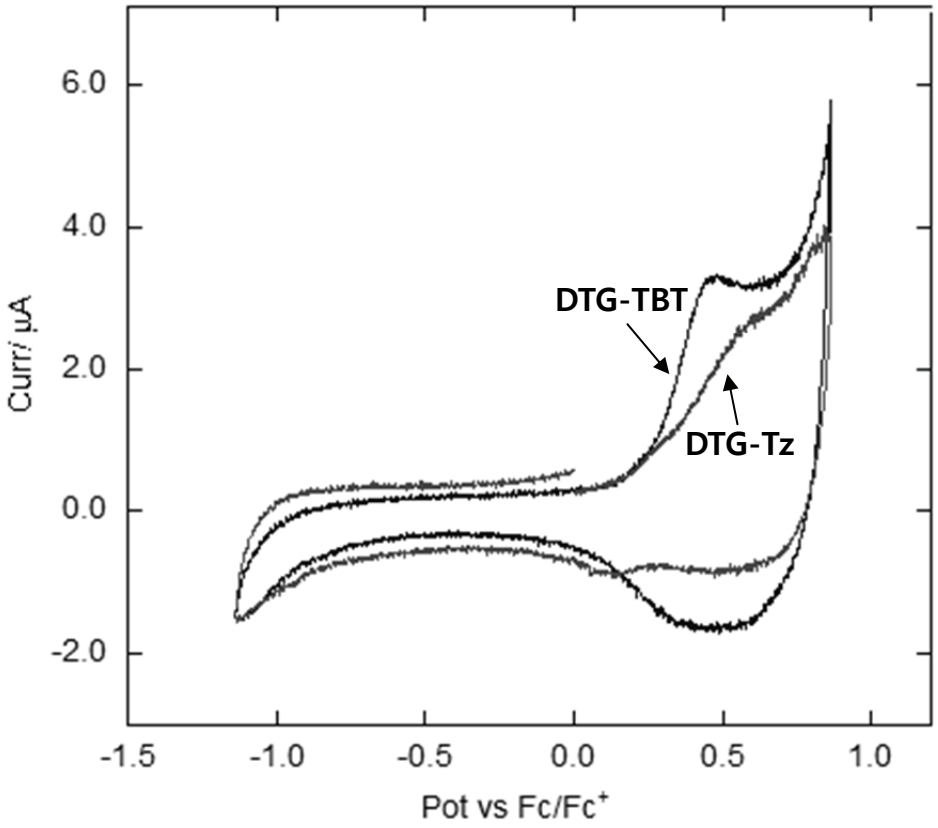
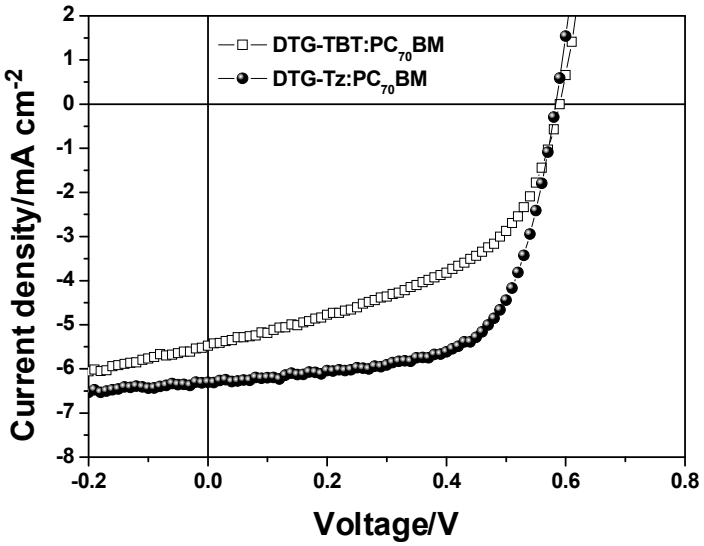


Figure 3. CVs of solid films of DTG-containing polymers.

a)



b)

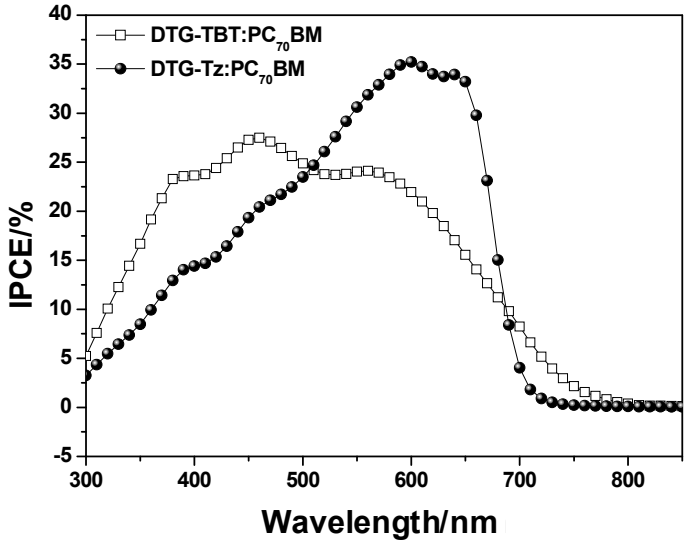


Figure 4. a) *J-V* and b) IPCE plots of DTG-polymer-based PSCs.