

Cite this: *RSC Adv.*, 2015, 5, 36673

Synthesis of D–A polymers with a disilanobithiophene donor and a pyridine or pyrazine acceptor and their applications to dye-sensitized solar cells†

Joji Ohshita,* Yohei Adachi, Daiki Tanaka, Makoto Nakashima and Yousuke Ooyama

New donor–acceptor polymers containing disilanobithiophene (DSBT) as the donor and pyridine or pyrazine as the acceptor with or without a thiophene spacer were prepared. The polymers showed UV-vis absorption maxima at $\lambda_{\text{max}} = 488\text{--}526\text{ nm}$, which were red-shifted relative to those of model monomers dithienylpyridine and dithienylpyrazine ($\lambda_{\text{max}} = 352\text{--}375\text{ nm}$), indicating the efficient conjugation along the polymer chains. A homo polymer of DSBT was also prepared. The DSBT-containing polymers were attached to TiO_2 electrodes by immersing the electrodes in the polymer solutions under irradiation ($>400\text{ nm}$) or in the dark. The modified electrodes were applied to dye-sensitized solar cells and a maximal power conversion efficiency of 0.89% was obtained using the TiO_2 electrode thermally modified with a DSBT–pyrazine alternating polymer.

Received 19th January 2015

Accepted 10th April 2015

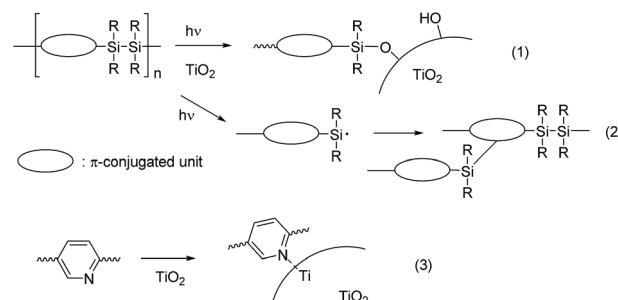
DOI: 10.1039/c5ra01055a

www.rsc.org/advances

Introduction

Conjugated donor–acceptor (D–A) compounds and polymers are of current interest because they possess optoelectronic functionalities, including photovoltaic properties.¹ Their broad and red-shifted absorption arising from their low band gaps make it possible to utilize the wide sunlight wavelength range, and their polar structures facilitate photo-induced charge separation in this system. Dye-sensitized solar cells (DSSCs) possess TiO_2 electrodes modified with sensitizing dyes. The dyes play a crucial role: electron injection from the photoexcited dyes into TiO_2 is the key step in the photocurrent generation.² The dyes usually have a D–A structure and an anchor unit, such as a carboxylic acid or a phosphoric acid, which forms an ester linkage with the TiO_2 surface. However, the ester linkages between the sensitizing dyes and the TiO_2 surface are generally labile and readily hydrolyzed by moisture, resulting in the detachment of the dyes from the TiO_2 surface. Recently, we introduced disilane as a new anchor group that reacts with the TiO_2 surface under UV irradiation to form a chemically and thermally stable Si–O–Ti linkage³ (Fig. 1(1)).⁴ In fact, irradiation of TiO_2 electrodes in solutions of poly(disilanyleneoligothienylene)s (**DSxT**, $x = 5$ or 6) led to the formation of polymer-attached electrodes (Chart 1) that could be used for

DSSCs.^{4a,b} However, DSSCs based on **DSxT** showed low performance, namely, a maximal power conversion efficiency (PCE) of 0.11%, which is likely due to their narrow absorption band in the visible region.^{4a} More recently, we prepared disilanylene polymers with conjugated D–A systems and used them as sensitizing dyes.^{4c,d} As expected, the introduction of the D–A structure into the polymer backbone improved DSSC performance due to the red-shifted broad absorption band, and resulted in a higher PCE of 0.25% (**pT₂Bt** in Chart 1).^{4c} The introduction of a pyridine (Py) unit into the polymer as the acceptor gave rise to an even higher DSSC performance (PCE = 0.40% for **pT₄Py**),^{4d} likely because the Lewis basic Py unit formed a complex with a Lewis acidic site of the TiO_2 surface providing secondary bonding that facilitated the dye attachment (Fig. 1(3)).⁵ However, in those systems, the photo-degradation of the disilanylene polymer by the addition of silyl radicals generated photochemically from the disilane units to the π -conjugated units competed with the formation of the

Fig. 1 Attachment of organosilicon polymer to TiO_2 surface.

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan. E-mail: jo@hiroshima-u.ac.jp; Fax: +81-82-424-5494; Tel: +81-824-424-7743

† Electronic supplementary information available: Experimental procedures of monomer syntheses, NMR spectra of the polymers, and molecular weight-dependent UV-vis spectra of **pDSBTTPzT2**. See DOI: 10.1039/c5ra01055a



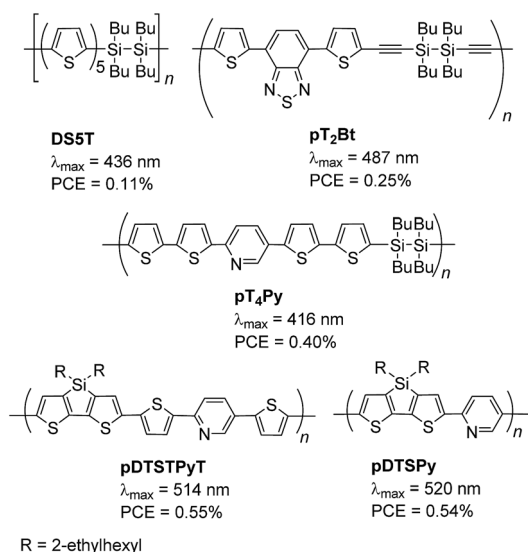


Chart 1 Previously reported organosilicon polymers as DSSC materials.

Si–O–Ti linkage to suppress the DSSC performance (Fig. 1(2)).⁶ Py polymers **pDTSTPyT** and **pDTSPy** without disilane bonds were then examined and found to show slightly higher PCEs of 0.55% and 0.54%, respectively.⁷

Recently, we introduced disilanobithiophene (DSBT) as a new donor component of conjugated D–A polymers, and demonstrated its application to bulk hetero-junction polymer solar cells.⁸ In this paper, we report the synthesis of new D–A polymers with DSBT donor and pyridine or pyrazine (Py or Pz) acceptor. Their optical properties and applications to DSSCs are described. The photochemically generated silyl radicals in DSBT would undergo facial recombination to recover the Si–Si bond, thereby avoiding their addition to the π -conjugated units. The Py and Pz units would coordinate to the Lewis acid center of TiO₂, thus making multiple binding of the polymer chain to the surface possible. We investigated also a homo polymer of DSBT to understand the roles of the Py and Pz units.

Experimental†

Synthesis of pDSBT

A mixture of 325 mg (0.405 mmol) of **DSBTBrSn**, 18.5 mg (5.0 mol%) of Pd₂(dba)₃, 24.7 mg (20.0 mol%) of P(*o*-tol)₃, and 8 mL of toluene was heated at 75 °C for 96 h. As a usual workup process, an aqueous solution of sodium *N,N*-diethylthiocarbamate trihydrate was added to the reaction mixture, and the mixture was heated at 80 °C for 2 h. The organic layer was separated and washed with water, 3 vol% acetic acid aqueous solution, and water again in that order. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated. The residue was reprecipitated from toluene/methanol and then toluene/ethanol to give 209 mg (92% yield) of **pDSBT** as a purple solid. Mp 209–258 °C. ¹H NMR (in C₆D₆): δ = 0.68–1.17 (20H, m, *n*Hex), 1.23–1.45 (24H, m, *n*Hex), 1.51–1.71 (8H, m, *n*Hex), 7.47 (2H, br s, thiophene).

¹³C NMR (in C₆D₆): δ = 13.48, 14.23, 16.25 (*n*HexSiO), 22.99, 23.47 (*n*HexSiO), 25.46, 31.84, 33.28 (*n*HexSiO), 33.69, 130.76, 135.94 (2C), 145.09.

Synthesis of pDSOBT

A mixture of 222 mg (0.272 mmol) of **DSOBTBrSn**, 12.5 mg (5.0 mol%) of Pd₂(dba)₃, 16.5 mg (20.0 mol%) of P(*o*-tol)₃, and 7 mL of toluene was heated at 75 °C for 96 h. After usual workup as above, the residue was reprecipitated from toluene/methanol to give 98.7 mg (63% yield) of **pDSOBT** as a red solid. Mp 110–158 °C. ¹H NMR (in C₆D₆): δ = 0.86–1.03 (20H, m, *n*Hex), 1.22–1.43 (24H, m, *n*Hex), 1.51–1.68 (8H, m, *n*Hex), 7.43 (2H, br s, thiophene). ¹³C NMR (in C₆D₆): δ = 14.29, 16.21, 22.93, 23.46, 31.92, 33.28, 131.08, 137.83, 140.31, 145.39.

Alternatively, **pDSOBT** was prepared by oxidizing **pDSBT**. A solution of 49.6 mg (0.446 mmol) of trimethylamine *N*-oxide dihydrate in 50 mL of toluene was dehydrated by azeotropic distillation of 10 mL of toluene. To this was added 81.5 mg of **pDSBT** at room temperature, and the mixture was heated to reflux overnight. After hydrolysis with water and evaporation of the solvent from the organic layer, the residue was reprecipitated from toluene/methanol to give **pDSOBT** as a red solid nearly quantitatively. Its ¹H NMR spectrum was consistent with that obtained by the polymerization of **DSOBTBrSn**.

Synthesis of DSBT-containing D–A polymers

A mixture of 342 mg (0.386 mmol) of **DSBTSn**, 91.6 mg (0.387 mmol) of 2,5-dibromopyridine, 17.4 mg (5.0 mol%) of Pd₂(dba)₃, 23.5 mg (20.0 mol%) of P(*o*-tol)₃, and 10 mL of chlorobenzene was heated at 75 °C for 96 h. After usual workup as was done for **pDSBT**, the residue was reprecipitated from toluene/methanol to give 203 mg (84% yield) of **pDSBTPy** as a red solid. Mp 64–87 °C. ¹H NMR (in CD₂Cl₂): δ = 0.70–1.08 (20H, m, *n*Hex), 1.16–1.48 (32H, m, *n*Hex), 7.14–7.24 (0.6H, br m, homo-coupled DSBT), 7.42 (0.7H, br s, DSBT), 7.62 (0.7H, br s, DSBT), 7.67–7.76 (0.7H, br m, pyridylene), 7.90 (0.7H, br s, pyridylene), 8.01–8.09 (0.2H, br m, terminal Br-pyridyl), 8.47–8.53 (0.2H, br m, terminal bromopyridyl), 8.85 (0.7H, br s, pyridylene), 8.97 (0.2H, br s, terminal bromopyridyl). ¹³C NMR (in C₆D₆): δ = 13.60, 14.21, 16.36 (*n*HexSiO), 22.99, 23.53 (*n*HexSiO), 25.53, 31.88, 33.34 (*n*HexSiO), 33.75. No clear sp² carbon signals were observed due to the broadening and the low solubility of the polymer.

Other DSBT-containing D–A type polymers were obtained in a fashion similar to that above. **pDSBTTPyT** was purified by reprecipitation from *o*-dichlorobenzene/methanol. Brown solid. Mp 201–211 °C. ¹H NMR (in C₆D₆): δ = 0.83–1.75 (52H, m, *n*Hex), 6.78–7.64 (8H, br m, aromatic protons), 8.80 (1H, br s, pyridylene). ¹³C NMR (in C₆D₆): δ = 13.58, 14.19, 22.98, 25.52, 31.87, 33.70. No clear sp² carbon signals were observed due to the broadening and the low solubility of the polymer. **pDSBTTPz** was purified by reprecipitation from hot toluene/methanol. Red solid. Mp 77–150 °C. ¹H NMR (in CD₂Cl₂): δ = 0.80–1.10 (20H, m, *n*Hex), 1.18–1.48 (32H, m, *n*Hex), 7.11–7.26 (0.4H, m, homo-coupled DSBT) 7.70 (2H, br s, thiophene), 8.90 (2H, br s, pyrazine). ¹³C NMR (in C₆D₆): δ = 13.57, 14.17, 16.33 (*n*HexSiO),

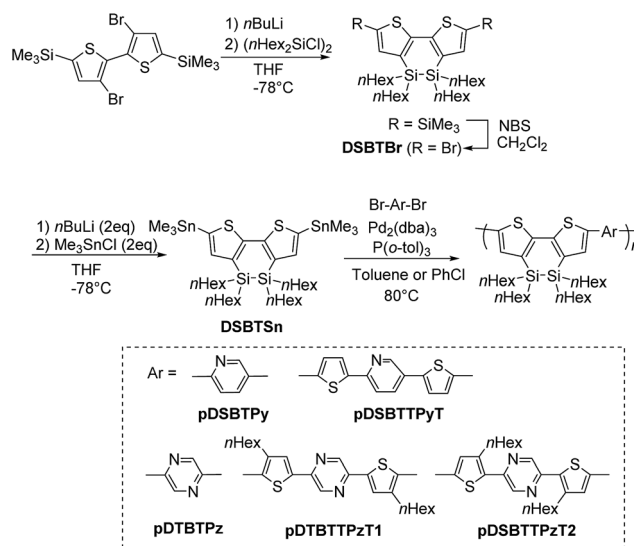


22.97, 23.53 (*n*HexSiO), 25.53, 31.88, 33.32 (*n*HexSiO), 33.72. No clear sp^2 carbon signals were observed due to the broadening and the low solubility of the polymer. **pDSBTTPzT1** was purified by reprecipitation from hot toluene/methanol. Red solid. Mp 200–226 °C. ^1H NMR (in C_6D_6): δ = 0.86–1.73 (74H, m, *n*Hex), 2.75–2.89 (4H, m, CH_2 on thiophene), 7.32 (2H, br s, DSBT thiophene), 7.56 (2H, s, thiophene), 8.64 (2H, s, pyrazine). ^{13}C NMR (in C_6D_6): δ = 13.52, 14.22, 14.25, 16.39 (*n*HexSiO), 22.29, 22.30, 23.55 (*n*HexSiO), 25.52, 29.61, 30.14, 30.82, 31.89, 32.05, 33.36 (*n*HexSiO), 33.73, 128.67, 132.96, 134.31, 135.23, 135.33, 139.64, 139.91, 141.41, 146.02, 146.32. **pDSBTTPzT2** was purified by reprecipitation from hot chlorobenzene/ethyl acetate. Brown solid. Mp 216–248 °C. ^1H NMR (in $\text{THF}-d_8$): δ = 0.70–1.99 (74H, m, *n*Hex), 2.93–3.16 (4H, br m, CH_2 on thiophene), 7.09–7.46 (4H, m, DSBT thiophene), 8.85 (2H, br s, pyrazine). ^{13}C NMR (in C_6D_6): δ = 13.57, 14.18, 22.98, 25.52, 29.55, 30.59, 31.86, 33.71. No clear sp^2 carbon signals were observed due to the broadening and the low solubility of the polymer.

Results and discussion

Polymer synthesis

We previously reported the synthesis of a DSBT-benzothiadiazole alternating polymer with butyl groups on the silicon atoms.⁸ In this study, we employed hexyl-substituted DSBT to increase the solubility of the polymers. Py-containing D–A polymers **pDSBTpy** and **pDSBTTPyT** were prepared by the Stille cross-coupling of **DSBTsn** with 2,5-dibromopyridine and 2,5-bis(5-bromo-2-thienyl)pyridine, respectively, as shown in Scheme 1 and Table 1. In those reactions, **DSBTsn** that was used as the monomer contained a small amount of the corresponding siloxane (DSOBT) that was formed during the preparation of **DSBTbr** and could not be separated from either **DSBTbr** or **DSBTsn**. The oxidation of DSBT units also occurred during the workup process of the polymers to an extent. The polymers were obtained as dark red solids and could be purified by reprecipitation. The lower yield of **pDSBTTPyT** than **pDSBTpy** was due to the formation of insoluble substances that were removed by filtration of the reaction mixture. Polymer molecular weights were determined by GPC (gel permeation chromatography) relative to polystyrene standards. GPC of **pDSBTTPyT** revealed a



Scheme 1 Synthesis of DSBT–Py and DSBT–Pz polymers.

bimodal GPC profile with maxima at approximate molecular weights of 7300 and 167 000, in contrast to **pDSBTpy** that showed a monomodal GPC profile. However, the origin of the different GPC profiles of the polymers is not clear yet. A DSBT homo polymer (**pDSBT**) was also prepared by the Stille coupling of **DSBTBrSn** as a purple solid (Scheme 2).

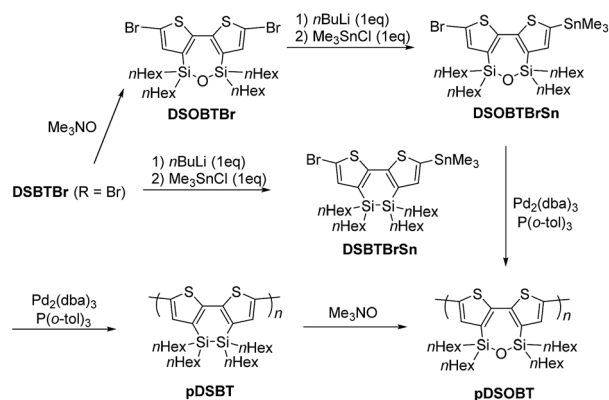
Polymer structures were verified mainly by NMR measurements.[†] The ^1H and ^{13}C NMR spectra of **pDSBTTPyT** were consistent with the regular alternating structure presented in Scheme 1. In contrast, those of **pDSBTpy** were rather complex, indicating structural irregularity. Fig. 2 shows the ^1H NMR spectrum of **pDSBTpy** with possible assignment based on the ^1H – ^1H COSY spectrum and comparison of the data with those of the monomers and related compounds, including **pDTSPy** and **pDSBT**. The spectrum revealed signals due to homo-coupled DSBT–DSBT units around 7.2 ppm. The incorporation ratio of the homo-coupled units was determined to be approximately $x/y = 75/25$ (Chart 2) on the basis of the signal integration. Similar homo-coupling was observed in the synthesis of **pDTSPy** under the same conditions.⁷ The spectrum also revealed small signals ascribed to terminal bromopyridyl units. The molecular weight calculated based on the integration of the terminal

Table 1 Synthesis of DSBT-containing polymers

Polymer	Yield/%	Siloxane ^a /%	GPC		UV absorption		TG ^c
			M_n	M_w/M_n	$\lambda_{\text{max}}/\text{nm}$	$\epsilon/\text{L g}^{-1} \text{cm}^{-1}$	
pDSBT	92	15	7200	1.95	542	3.0×10^4	425
pDSOBT	63	100	8000	2.07	488	2.7×10^4	454
pDTBTpy	77	13	9500	1.86	489	3.1×10^4	419
pDSBTTPyT	8	— ^b	8700	9.50	514	5.9×10^4	445
pDTBTpz	75	22	8400	2.17	522	5.4×10^4	445
pDSBTTPzT1	80	3	21 400	2.30	517	6.9×10^4	443
pDSBTTPzT2	69	— ^b	37 800	4.55	526	5.9×10^4	437

^a Siloxane contamination in the backbone, based on ^{13}C NMR spectra. ^b Could not be determined due to low solubility, but siloxane contamination could be detected by IR spectrum. ^c In nitrogen at the heating rate of $10^\circ\text{C min}^{-1}$.

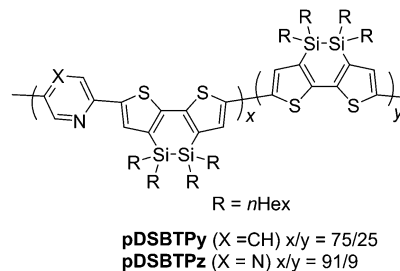




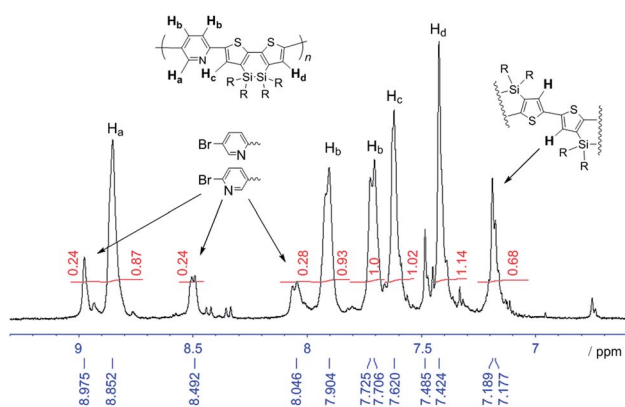
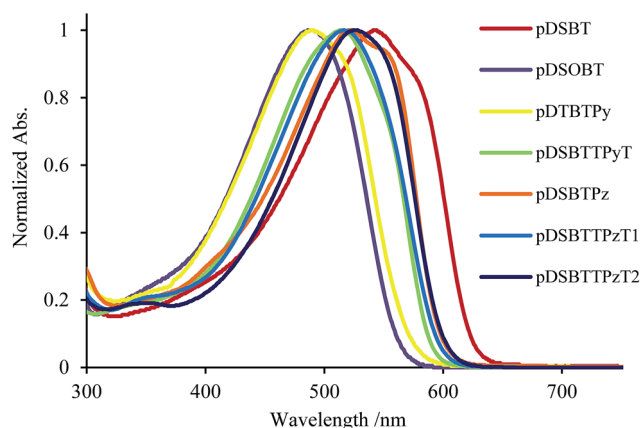
Scheme 2 Synthesis of DSBT homo polymer and its oxidation.

bromopyridyl protons was approximately 7000, in good agreement with that determined by GPC. The contamination ratio of siloxane units in **pDSBTpy** was determined from the intensities of the hexyl groups in the ^{13}C NMR spectra. The siloxane hexyl carbon signals were identified by comparison with those of **pDSOBT** that was prepared in two routes, as shown in Scheme 2. The broad Si–O stretching band around 1000 cm^{-1} in the IR spectra also indicated the existence of the siloxane bonds. For **pDSBTTPyT**, no homo-coupled units were detected by NMR analysis. Siloxane contamination in **pDSBTTPyT** was noted from the IR spectrum, but the ratio could not be determined from the ^{13}C NMR spectrum due to the low solubility of the polymer.

As shown in Table 1 and Fig. 3, the present polymers exhibited broad absorption bands in the UV-vis region, which were red-shifted from those of **DSBTBr** ($\lambda_{\text{max}} = 356\text{ nm}$) and **TPyT** (Chart 3), indicating the efficient conjugation between DSBT and Py or TPyT units. However, the absorption bands were blue-shifted from that of **pDSBT**. The twisting of the DSBT–Py bonds, which arose from the steric repulsion between thiophene and Py C–H bonds, seemed to be responsible for the suppressed conjugation of **pDSBTpy** and **pDSBTTPyT**. In fact, computation on models at the B3LYP/6-31G(d) level of theory

Chart 2 Detailed structures of **pDSBTpy** and **pDSBTpz**.

indicated a larger dihedral angle between the π -conjugated units of DSBT–Py than that of DSBT–DSBT, as shown in Fig. 4a. The rather weak D–A interaction arising from the limited electron-accepting properties of Py would be also one reason for the blue-shifted absorption of the Py polymers. As depicted in Fig. 4b, both the HOMO and LUMO are delocalized over the DSBT–Py π -system, although the HOMO seems to be more DSBT-like judging from that the HOMO energy level is close to that of the DSBT unit. Similarly, an analogous DTS polymer **pDTSPy** has been reported to exhibit blue-shifted absorption ($\lambda_{\text{max}} = 520\text{ nm}$) relative to that of a DTS homo polymer ($\lambda_{\text{max}} = 535\text{ nm}$).⁷ The absorption maxima of the present DSBT-polymers were also found at higher energies than those of the corresponding dithienosilole polymers, **pDTSPy** and **pDTSTPyT** ($\lambda_{\text{max}} = 519\text{ nm}$). This may be due to the contamination of siloxane units in polymers **pDSBTpy** and **pDSBTTPyT**. It has been demonstrated that the conjugation in the silicon-bridged bithiophene is suppressed in the order of DTS⁹ \approx DSBT¹⁰ > DSOBT,¹¹ depending on the electronic effects of the silicon bridges and the planarity of the bithiophene units (Chart 3). Compared with DTS, DSBT possesses a more twisted bithiophene but exhibits stronger interaction between the silicon σ^* -orbital and the bithiophene π^* -orbital, thereby lowering LUMO and providing a similar degree of conjugation, as shown in Fig. 4b.^{8,12} It is also seen that the Si–Si σ -orbital also contributes the HOMO to elevate it. It is also noteworthy that

Fig. 2 ^1H NMR spectrum of **pDSBTpy** in CD_2Cl_2 with possible assignments ($\text{sp}^2\text{ CH}$ region).Fig. 3 UV-vis spectra of DSBT-containing polymers in dichlorobenzene or chloroform (for **pDSBTTPyT**).

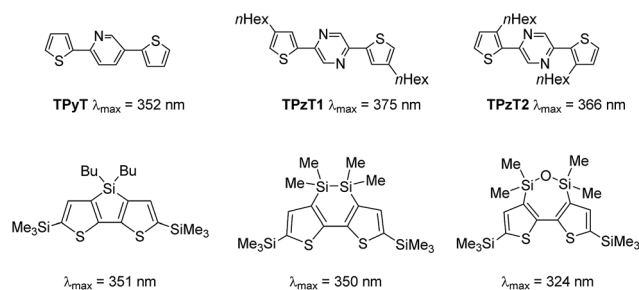


Chart 3 UV-vis absorption maxima of dithienylpyridine and dithienylpyrazine, and silicon-bridged bithiophenes.

compared with conventional polythiophenes, **pDSBT** showed expanded conjugation in a manner similar to **pDTS** ($\lambda_{\text{max}} = 545\text{--}561 \text{ nm}$), *e.g.*, regio-regular poly(3-hexylthiophene) showed an absorption maximum at 458 nm .¹³

We prepared Pz-containing polymers **pDSBTpZ**, **pDSBTpZT1**, and **pDSBTpZT2**, with the expectation that replacement of the Py unit by a sterically less hindered Pz unit would enhance the polymer planarity (Scheme 1). For TPzT units, we introduced solubilizing hexyl groups. As expected, the Pz polymers showed red-shifted absorption maxima relative to those of model monomers **TPzT1** and **TPzP2** (Chart 3) and Py polymers **pDSBTpy** and **pDSBTTPyT**. Higher molecular weight of **pDSBTpZT1**, and **pDSBTpZT2** may also be responsible for the red-shifted maxima from that of **pDSBTTPyT**. In fact, **pDSBTpZT2** with low molecular weight ($M_n = 3800$ and $M_w/M_n = 12.2$) that was separated from the polymerization mixture as a solid soluble in ethyl acetate gave rise to a blue-shifted absorption maximum at 514 nm .[†] However, this was still nearly the same as that of **pDSBTTPyT** with higher molecular weight $M_n = 8700$ and $M_w/M_n = 9.5$, indicative of that Pz-containing polymers possess essentially the more enhanced conjugation. The introduction of alkyl groups on the polymers led to the increased solubility and thus the higher molecular weights of **pDSBTpZT1** and **pDSBTpZT2** than that of **pDSBTTPyT**. They showed monomodal profile in GPC analysis.

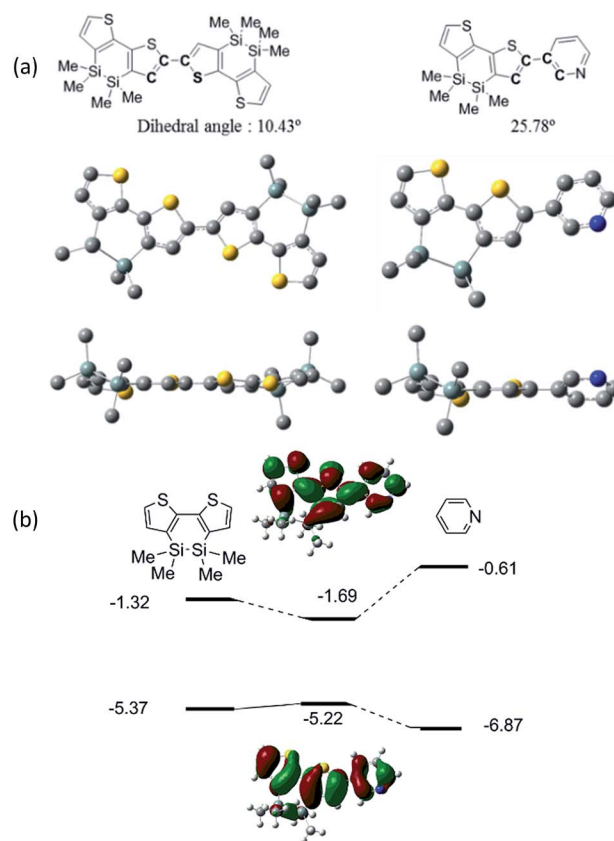


Fig. 4 (a) Dihedral angles and optimized geometries of DSBT-DSBT (left) and DSBT-Py (right) models with methyls on silicon atoms at B3LYP/6-31G(d) (hydrogen atoms are omitted for clarity). (b) HOMO and LUMO energy levels and profiles of DSBT-Py model.

The ^1H NMR spectrum of **pDSBTpZ** confirmed the existence of the homo-coupled units, similarly to **pDSBTpy**. However, the incorporation ratio was only $x/y = 91/9$ (Chart 2), which was much smaller than that of **pDSBTpy**. It is likely that the formation of sterically less hindered DSBT-Pz bonds proceeded more smoothly than the formation of DSBT-Py bonds. No

Table 2 DSSC^a performance based on DSBT-containing polymers

Polymer	Method ^b	Abs max ^c /nm	V_{oc} /mV	J_{sc} /mA cm ⁻²	FF	PCE (η)/%
pDSBT	P	451	308	2.10	0.61	0.39
	T	520	356	0.69	0.67	0.16
pDSBTpy	P	439	344	1.91	0.63	0.41
	T	484	396	1.67	0.63	0.42
pDSBTTPyT	P	468	380	3.11	0.63	0.74
	T	475	392	1.34	0.66	0.35
pDSBTpZ	P	468	384	1.58	0.62	0.38
	T	496	424	3.22	0.65	0.89
pDSBTpZT1	P	482	396	2.21	0.64	0.56
	T	489	432	2.28	0.68	0.67
pDSBTpZT2	P	490	384	2.70	0.59	0.61
	T	503	420	1.58	0.66	0.44

^a Cell structure: FTO/polymer-attached $\text{TiO}_2/\text{I}^-/\text{Pt}$. ^b P: under irradiation, T: in the dark. ^c UV-vis absorption maximum of polymer-attached electrode.



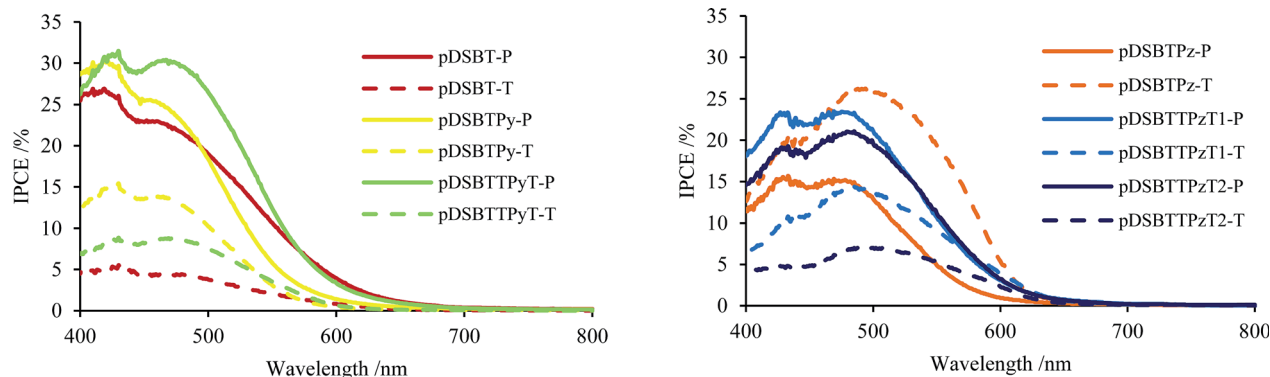


Fig. 5 IPCE spectra of TiO_2 electrodes modified with DSBT-polymers (P: photochemical conditions, T: thermal conditions).

signals due to the homo-coupled units were observed in the ^1H NMR spectra of **pDSBTTPzT1** and **pDSBTTPzT2**.

The thermal stability of the polymers was investigated by thermogravimetric analysis (TGA) in nitrogen and the 5% weight loss temperatures are listed in Table 1. Thermal decomposition occurred at temperatures exceeding 400°C , indicating the good thermal stability of the present polymers.

Applications to DSSCs

To prepare polymer-attached electrodes, TiO_2/FTO electrodes were immersed in chloroform solutions of the present polymers (3 mg mL^{-1}) in argon for 40 min under irradiation ($>400\text{ nm}$) (photochemical conditions) or in the dark (thermal conditions). Homo polymer **pDSBT** attached to the TiO_2 surface efficiently under irradiation, providing a brown electrode. On the other hand, a lightly coloured electrode was obtained in the dark, indicating that the photochemical reactions of **pDSBT** occurred efficiently on the TiO_2 surface, likely by forming Si–O–Ti bonds, although the thermal attachment of the polymer to TiO_2 would be also involved to a certain extent. Alternating polymers with Lewis basic Py or Pz units could readily attach to the TiO_2 electrodes under both photochemical and thermal conditions. No evident colour difference depending on the conditions was seen. However, the UV-vis spectra of the photochemically modified electrodes always showed blue-shifted absorption bands relative

to those of the thermally modified electrodes (Table 2), indicating the photodegradation of chromophores. The Ti–O–Si bond formation would enhance the twisting of bithiophene units. The polymer-attached electrodes were then used for DSSCs with the $\text{FTO}/\text{polymer-attached TiO}_2/\text{I}^-/\text{I}_3^-/\text{Pt}$ structure. All the polymers exhibited sensitizing effects (Fig. 5 and 6) and the cell parameters are summarized in Table 2. The cell with **pDSBT** showed higher performance when TiO_2 was photochemically modified, probably due to the higher degree of polymer attachment. For the cells with Py- or Pz-containing polymers, however, no clear relationship between the performance and the attachment conditions was observed. For some of those cells, it is presumed that sufficient amounts of the polymers could be attached even in the dark. The highest performance was obtained using the electrode thermally modified by **pDSBT-Pz**.

Quantum chemical simulation for polymer reaction

To understand the anchoring reaction of DSBT with the TiO_2 surface, we carried out quantum chemical calculations at the B3LYP/6-31+G(dp) level of theory on the Gaussian 09 program, and the results are presented in Fig. 7. The reaction was an exothermic one ($-50.1\text{ kcal mol}^{-1}$), likely due to the formation of thermodynamically stable Si–O bonds. The optimized geometries of DSBT and DSBT-attached TiO_2 models indicate that the attachment enhances the twisting of the bithiophene

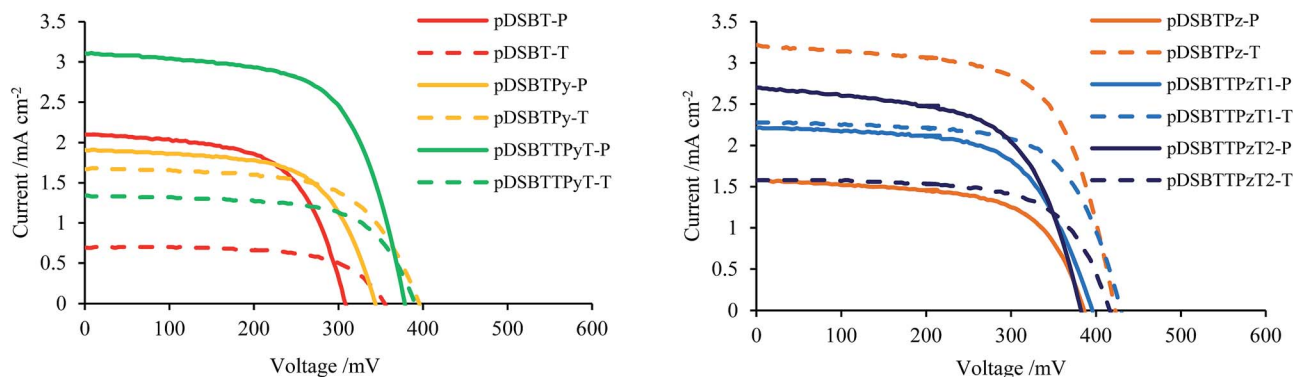


Fig. 6 I - V characteristics of DSSCs based on TiO_2 electrodes modified with DSBT polymers (P: photochemical conditions, T: thermal conditions).



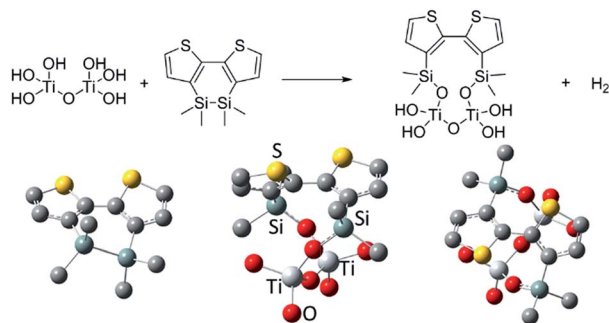


Fig. 7 Model reaction (top) and optimized geometries (bottom) of DSBT and top and side views of DSBT-attached TiO_2 models (from left to right), derived from quantum chemical simulation at B3LYP/6-31+G(dp) (hydrogen atoms are omitted for clarity).

system in which the S–C–C–S dihedral angle is increased from 19.1° to 68.8° . This may be the reason for the blue-shifted absorption of the polymers upon interaction with the TiO_2 surface even under thermal conditions.

Conclusions

In summary, we prepared new D–A polymers with DSBT as the donor and Py or Pz as the acceptor, and applied them to DSSCs. Although the device performance is still unsatisfactory, this is a new polymer system that is expected to modify inorganic oxide surfaces. Studies to explore polymer functionalities other than DSSC applications are in progress.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (B) (no. 26288094) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Notes and references

- 1 Y.-J. Cheng, S.-H. Yang and C.-S. Hsu, *Chem. Rev.*, 2009, **109**, 5868.

- 2 Y. Ooyama and Y. Harima, *Eur. J. Org. Chem.*, 2009, **18**, 2903.
- 3 (a) K. Kakiage, M. Yamamura, E. Fujimura, T. Kyomen, M. Unno and M. Hanaya, *Chem. Lett.*, 2010, **39**, 260; (b) M. Unno, K. Kakiage, M. Yamamura, T. Kogure, T. Kyomen and M. Hanaya, *Appl. Organomet. Chem.*, 2010, **24**, 247.
- 4 (a) J. Ohshita, J. Matsukawa, M. Hara, A. Kunai, S. Kajiwar, Y. Ooyama, Y. Harima and M. Kakimoto, *Chem. Lett.*, 2008, **37**, 316; (b) J. Ohshita, D. Tanaka, J. Matsukawa, T. Mizumo, H. Yoshida, Y. Ooyama and Y. Harima, *Chem. Lett.*, 2011, **40**, 87; (c) D. Tanaka, J. Ohshita, Y. Ooyama, T. Mizumo and Y. Harima, *J. Organomet. Chem.*, 2012, **719**, 30; (d) D. Tanaka, J. Ohshita, T. Mizumo, Y. Ooyama and Y. Harima, *J. Organomet. Chem.*, 2013, **741–742**, 97.
- 5 Y. Ooyama, S. Inoue, T. Nagano, K. Kushimoto, J. Ohshita, I. Imae, K. Komaguchi and Y. Harima, *Angew. Chem., Int. Ed.*, 2011, **50**, 7429.
- 6 (a) J. Ohshita and A. Kunai, *Acta Polym.*, 1998, **49**, 379; (b) A. Kunai, T. Ueda, K. Horata, E. Toyoda, I. Nagamoto, J. Ohshita, M. Ishikawa and K. Tanaka, *Organometallics*, 1996, **15**, 2000; (c) J. Ohshita, D. Kanaya and M. Ishikawa, *J. Organomet. Chem.*, 1994, **468**, 55.
- 7 D. Tanaka, J. Ohshita, Y. Ooyama and Y. Morihara, *Polym. J.*, 2013, **45**, 1153.
- 8 J. Ohshita, M. Nakashima, D. Tanaka, Y. Morihara, H. Fueno and K. Tanaka, *Polym. Chem.*, 2014, **5**, 346.
- 9 D.-H. Kim, J. Ohshita, K.-H. Lee, Y. Kunugi and A. Kunai, *Organometallics*, 2006, **25**, 1511.
- 10 J. Ohshita, M. Nodono, H. Kai, T. Watanabe, A. Kunai, K. Komaguchi, M. Shiotani, A. Adachi, K. Okita, Y. Harima, K. Yamashita and M. Ishikawa, *Organometallics*, 1999, **18**, 1453.
- 11 Y.-W. Kwak, I.-S. Lee, M.-K. Baek, U. Lee, H.-J. Choi, M. Ishikawa, A. Naka, J. Ohshita, K.-H. Lee and A. Kunai, *Organometallics*, 2006, **25**, 48.
- 12 H. Kai, J. Ohshita, S. Ohara, N. Nakayama, A. Kunai, I.-S. Lee and Y.-W. Kwak, *J. Organomet. Chem.*, 2008, **693**, 3490.
- 13 J. Ohshita, K. Kimura, K.-H. Lee, A. Kunai, Y.-W. Kwak, E.-C. Son and Y. Kunugi, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 4588.

