

Supporting information

Synthesis of organic photosensitizers containing dithienogermole and thiadiazolo[3,4-c]pyridine units for dye-sensitized solar cells

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Experimental

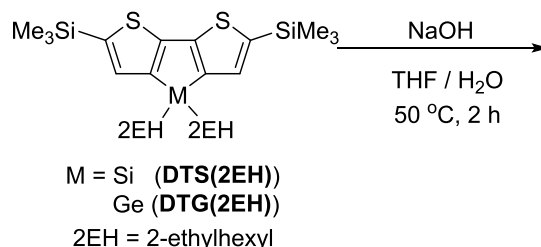
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Experimental

General

All reactions were carried out under dry argon. For the reaction solvents, THF, DMF, toluene, chloroform, dichloromethane were purchased from Kanto Chemical Co. Ltd. They were distilled from calcium hydride and stored over activated molecular sieves until use, while chloroform and dichloromethane were distilled from calcium hydride immediately before use. Usual workup mentioned below includes hydrolysis of the reaction mixture with water and separation of the organic layer. The aqueous layer was extracted with toluene, chloroform, hexane or ethyl acetate. The organic layer and the extract were combined and washed with water. After drying over anhydrous magnesium sulfate, the solvent was evaporated. Starting materials, **DTGBr** [S1], 4-(trimethylstannyl)triphenylamine [S2], **PTzBr2** [S3], 4-(thiophen-2-yl)-pyridine [S4], and 4,4,5,5-tetramethyl-2-[5-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)thiophen-2-yl]-1,3,2-dioxaborolane (**a-3**) [S5] were prepared according to the literature methods.

Control experiment



A mixture of 52.6 mg (93.4 μmol) of **DTS(2EH)** or 60.3 mg (99.2 μmol) of **DTG(2EH)**, 2.0 mL of 1M NaOH aq, and 2.0 mL of THF was heated at 50 °C for 2 h with stirring. After the mixture was cooled to room temperature, the usual workup gave the residue, which was characterized by ^1H , ^{13}C , ^{29}Si NMR and HR-mass spectrometry.

Data for [5,5'-bis(trimethylsilyl)-3-(2,2'-bithienyl)]bis(2-ethylhexyl)silanol (diastereomeric mixture):

^1H NMR (in CDCl_3): δ = 0.32 (18H, s, Me_3Si), 0.70-0.90 (12H, m, CH_3), 1.10-1.30 (20H, m, CH_2),

1.40-1.50 (2H, m, CH), 7.15 (1H, d, $J = 3.2$ Hz, thiophene), 7.20 (1H, d, $J = 3.2$ Hz, thiophene), 7.27 (1H, s, thiophene). ^{13}C NMR (in CDCl_3): $\delta = -0.1, -0.1, -0.0, -0.0, 10.6, 14.1, 22.0, 22.0, 22.0, 22.1, 22.9, 23.0, 28.1, 28.7, 28.8, 34.8, 34.8, 35.6, 35.6, 128.4, 142.5, 128.5, 128.5, 128.5, 128.6, 134.2, 134.2, 134.3, 134.3, 138.9, 138.9, 138.9, 140.7, 140.7, 140.7, 140.8, 140.8, 141.8, 142.6, 147.7, 147.7, 147.7$. ^{29}Si NMR (in CDCl_3): $\delta = -6.9, -6.6, 5.9, 6.0, 6.1$. HR-MS (APCI) Calcd for $\text{C}_{30}\text{H}_{56}\text{OS}_2\text{Si}_3$: $[\text{M}+\text{H}]^+$: 580.30749, Found: 580.30872.

No reaction took place for **DTG(2EH)**.

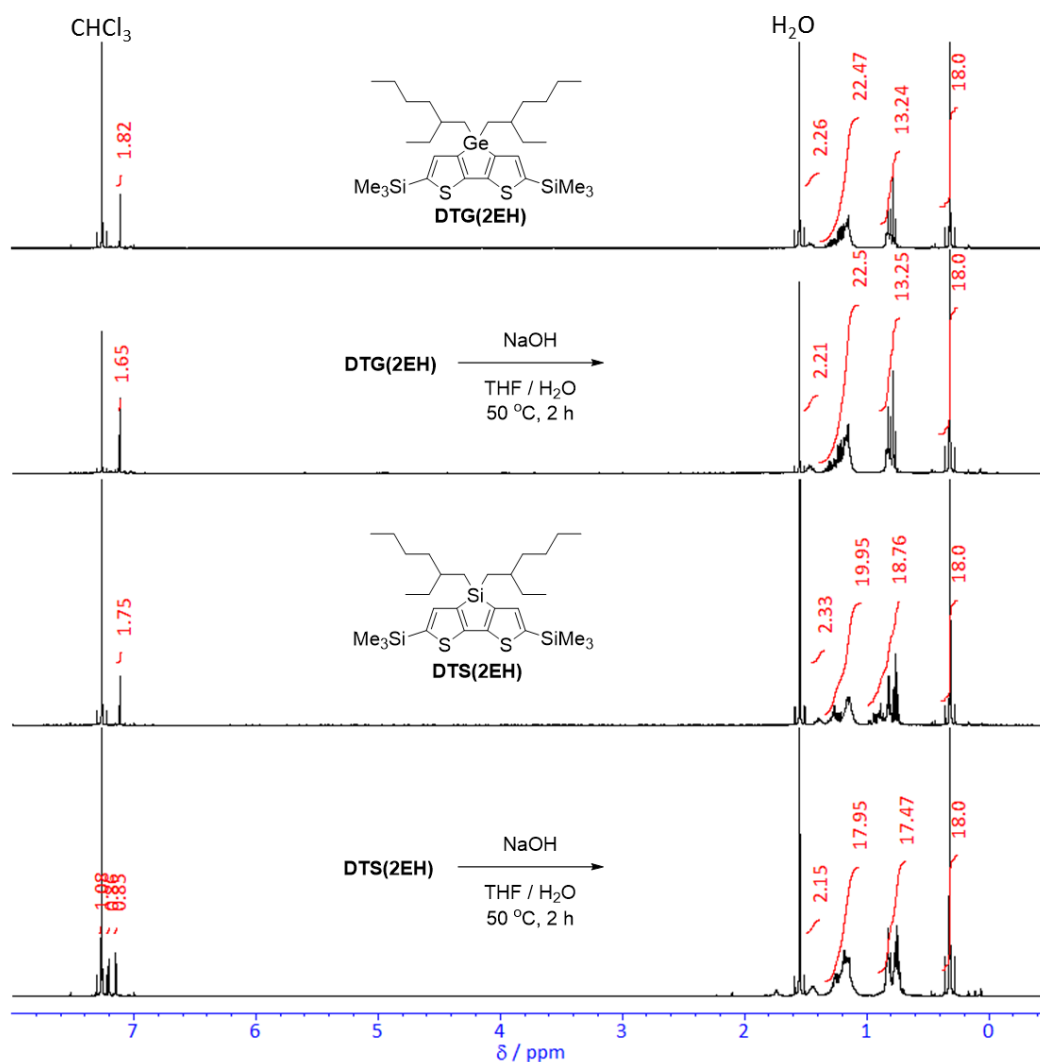
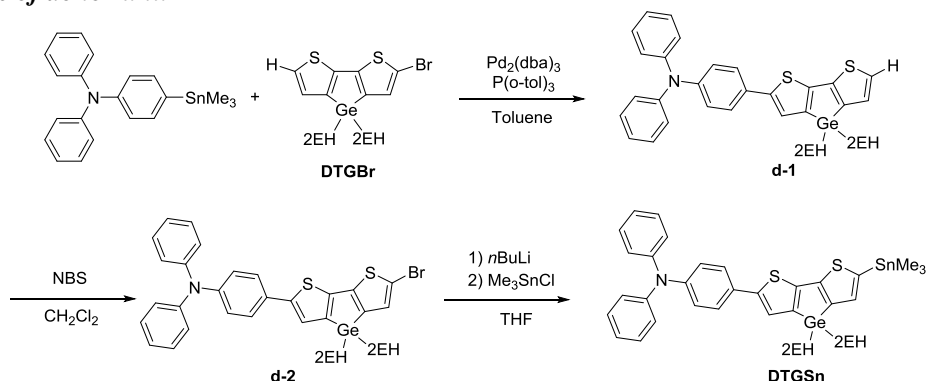


Figure S1 Full-scale ^1H NMR spectra of **DTG(2EH)** and **DTS(2EH)** before and after hydrolysis.

Synthesis of donor unit



Synthesis of 4-[4,4-Bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]germol-2-yl]phenyl-N,N-diphenylamine (**d-1**) (diastereomeric mixture)

A mixture of 1.48 mmol of 4-(trimethylstannyl)phenyldiphenylamine, 803 mg (1.48 mmol) of DTGBr, 27.8 mg (2.0 mol%) of $\text{Pd}_2(\text{dba})_3$, 46.0 mg (10 mol%) of $\text{P}(o\text{-tol})_3$, and 20 mL of toluene was heated at 100 °C for 1.5 day with stirring. After usual workup using toluene for extraction, the residue was subjected to silica gel chromatography eluting with hexane/chloroform = 1/1, then preparative GPC eluting with toluene to give 661 mg (0.935 mmol, 63% yield) of **d-1** as a yellow oil: ^1H NMR (in CD_2Cl_2): δ = 0.82-0.90 (12H, m, CH_3), 1.20-1.43 (20H, m, CH_2), 1.54-1.62 (2H, m, CH), 7.06-7.12 (4H, m, *p*-Ph and phenylene), 7.13-7.18 (5H, m, DTG and *o*-Ph), 7.27 (1H, d, J = 4.4 Hz, DTG), 7.29 (1H, s, DTG), 7.29-7.34 (4H, m, *m*-Ph), 7.53 (2H, d, J = 8.4 Hz, phenylene). ^{13}C NMR (in CD_2Cl_2): δ = 11.2, 14.4, 21.1, 23.5, 29.16, 29.18, 29.40, 29.42, 35.91, 35.94, 37.5, 123.5, 124.3, 124.9, 125.3, 125.6, 126.7, 129.4, 129.8, 130.4, 143.86, 143.95, 144.04, 144.85, 144.87, 144.89, 145.20, 145.22, 145.23, 145.96, 146.04, 146.1, 146.83, 146.86, 146.89, 147.4, 148.0. HR-MS (APCI) Calcd for $\text{C}_{42}\text{H}_{51}\text{GeNS}_2$: $[\text{M}+\text{H}]^+$: 708.27475, Found: 708.27521.

Synthesis of 4-[4,4-Bis(2-ethylhexyl)-6-bromodithieno[3,2-b:2',3'-d]germol-2-yl]phenyl-N,N-diphenylamine (**d-2**) (diastereomeric mixture)

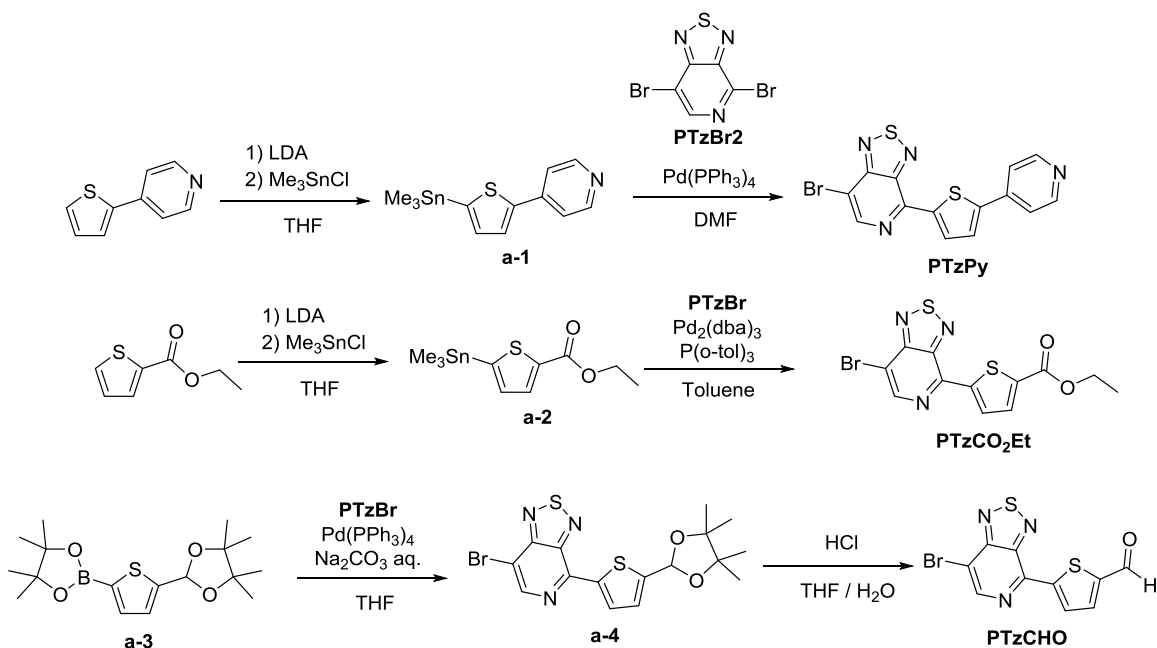
To a solution of 167 mg (0.237 mmol) of **d-1** in 10 mL of dichloromethane was added 42.2 mg (0.237 mmol) of NBS in several portions and the mixture was stirred at room temperature for 1 h with stirring.

After usual workup using chloroform for extraction, the residue was subjected to preparative GPC eluting with toluene to give 148 mg (0.188 mmol, 79% yield) of **d-2** as a yellow oil: ^1H NMR (in CD_2Cl_2): δ = 0.80-0.91 (12H, m, CH_3), 1.15-1.35 (20H, m, CH_2), 1.49-1.57 (2H, m, CH), 7.04-7.09 (5H, m), 7.13 (4H, dd, J = 8.8, 1.2 Hz, *o*-Ph), 7.27 (1H, s, DTG), 7.27-7.32 (4H, m, *m*-Ph), 7.48 (2H, d, J = 8.4 Hz, phenylene). ^{13}C NMR (in CD_2Cl_2): δ = 11.11, 11.13, 14.4, 21.11, 21.14, 23.4, 23.5, 29.16, 29.19, 29.3, 29.4, 35.85, 35.88, 37.41, 37.43, 110.66, 110.67, 110.69, 123.6, 124.1, 124.9, 125.5, 126.7, 129.0, 129.7, 133.1, 144.1, 144.2, 144.27, 144.34, 144.36, 144.39, 145.1, 145.2, 145.3, 145.42, 145.44, 145.46, 147.42, 147.44, 147.46, 147.53, 147.9. HR-MS (APCI) Calcd for $\text{C}_{42}\text{H}_{50}\text{BrGeNS}_2$: M^+ : 785.17743, Found: 785.17847.

Synthesis of 4-[4,4-Bis(2-ethylhexyl)-6-(trimethylstannyl)dithieno[3,2-b:2',3'-d]germol-2-yl]phenyl-N,N-diphenylamine (DTGSn) (diastereomeric mixture)

To a solution of 682 mg (0.868 mmol) of **d-2** in 20 mL of THF was added 0.70 mL (1.11 mmol) of a solution of 1.58 M *n*-butyllithium in hexane at -78 °C over a period of 30 min and the mixture was stirred at this temperature for 30 min with stirring. To this was added 226 mg (1.13 mmol) of trimethyltin chloride at this temperature and the mixture was stirred at room temperature overnight. After usual workup using hexane for extraction, the residue was subjected to preparative GPC eluting with toluene to give 339 mg (0.390 mmol, 45% yield) as a yellow oil: ^1H NMR (in CD_2Cl_2): δ = 0.42 (9H, s, Me_3Sn), 0.80-0.94 (12H, m, CH_3), 1.17-1.40 (20H, m, CH_2), 1.50-1.60 (2H, m, CH), 7.02-7.13 (4H, m, *p*-Ph and phenylene), 7.14 (4H, dd, J = 8.4, 1.2 Hz, *o*-Ph), 7.18 (1H, s, DTG), 7.26 (1H, s, DTG), 7.27-7.33 (4H, m, *m*-Ph), 7.51 (2H, d, J = 8.8 Hz, phenylene). ^{13}C NMR (in CD_2Cl_2): δ = -8.0, 11.18, 11.22, 14.5, 21.1, 21.2, 23.51, 23.52, 29.3, 29.4, 29.5, 35.9, 36.0, 37.5, 37.6, 123.5, 124.3, 124.9, 125.8, 126.7, 129.6, 129.8, 138.4, 144.68, 144.70, 144.72, 145.37, 145.40, 145.43, 145.45, 145.51, 145.9, 146.0, 146.2, 147.4, 148.1, 152.6. HR-MS (APCI) Calcd for $\text{C}_{45}\text{H}_{59}\text{GeNS}_2\text{Sn}$: $[\text{M}+\text{H}]^+$: 872.23954, Found: 872.24005.

Synthesis of acceptor unit



Synthesis of 4-[5-(Trimethylstannyl)-2-thienyl]pyridine (**a-1**)

To a solution of 324 mg (2.01 mmol) of 4-(2-thienyl)pyridine in 10 mL of THF was added 1.8 mL (2.03 mmol) of a solution of 1.13 M LDA in hexane/THF at -78 °C over a period of 10 min and the mixture was stirred at this temperature for 1 h. To this was added 422 mg (2.12 mmol) of trimethyltin chloride at this temperature and the mixture was stirred at 35 °C for 30 min. After usual workup using ethyl acetate for extraction, 634 mg (1.96 mmol, 98% yield) of **a-1** was obtained as a light brown solid. The crude product was analyzed by ¹H, ¹³C NMR and MS spectrometry used for the following reaction without further purification: ¹H NMR (in CDCl₃): δ = 0.41 (9H, s, Me₃Sn), 7.21 (1H, d, *J* = 3.2 Hz, thiophene), 7.46-7.49 (2H, m, pyridyl), 7.59 (1H, d, *J* = 3.2 Hz, thiophene), 8.55-8.58 (2H, m, pyridyl). ¹³C NMR (in CDCl₃): δ = -8.2, 119.9, 126.4, 136.4, 141.2, 141.3, 146.7, 150.3. HR-MS (APCI) Calcd for C₁₂H₁₅NSSn: [M+H]⁺: 326.00199, Found: 326.00214.

Synthesis of 7-Bromo-4-[5-(4-pyridyl)-2-thienyl][1,2,5]thiadiazolo[3,4-c]pyridine (**PTzPy**)

A mixture of 283 mg (0.959 mmol) of **PTzBr2**, 320 mg (0.988 mmol) of **a-1**, 185 mg (15 mol%) of

Pd(PPh₃)₄, and 10 mL of DMF was heated at 120 °C for 1 h. After usual workup using chloroform for extraction, the residue was purified by preparative GPC eluting with chloroform to give 80.2 mg (0.214 mmol, 22% yield) of **PTzPy** as an orange powder: S.p.: 250 °C. ¹H NMR (in CDCl₃): δ = 7.63-7.65 (2H, m, pyridyl), 7.65 (1H, d, *J* = 4.0 Hz, thiophene), 8.66-8.69 (2H, m, pyridyl), 8.71 (1H, s, PTz), 8.71 (1H, d, *J* = 4.0 Hz, thiophene). ¹³C NMR spectrum was not obtained because of low solubility of the product. HR-MS (APCI) Calcd for C₁₄H₇BrN₄S₂: [M+H]⁺: 374.93683, Found: 374.93765.

Synthesis of Ethyl 5-(trimethylstannyl)thiophene-2-carboxylate (a-2)

Compound **a-2** was obtained from ethyl thiophene-2-carboxylate in a fashion similar to that of **a-1** as a brown liquid in 92% yield. The ¹H and ¹³C NMR spectra of the crude product showed its purity higher than 95% and the crude product was used for the following reaction without further purification: ¹H NMR (in CDCl₃): δ = 0.40 (9H, s, Me₃Sn), 1.37 (3H, t, *J* = 6.8 Hz, CH₃), 4.34 (2H, q, *J* = 6.8 Hz, CH₂), 7.17 (1H, d, *J* = 3.6 Hz, thiophene), 7.87 (1H, d, *J* = 3.6 Hz, thiophene). ¹³C NMR (in CDCl₃): δ = -8.3, 14.4, 60.9, 133.9, 135.4, 139.2, 147.6, 162.1. HR-MS (ESI) Calcd for C₁₀H₁₆O₂SSn: [M+Na]⁺: 342.97852, Found: 342.97845.

Synthesis of Ethyl 5-(7-bromo[1,2,5]thiadiazolo[3,4-c]4-pyridyl)thiophene-2-carboxylate (PTzCO₂Et)

A mixture of 362 mg (1.23 mmol) of **PTzBr2**, 204 mg (1.30 mmol) of **a-2**, 61.2 mg (5 mol%) of Pd₂(dba)₃, 74.6 mg (20 mol%) of P(*o*-tol)₃, and 13 mL of toluene was heated at 60 °C for 5 h with stirring. After usual workup using chloroform for extraction, the residue was purified by preparative GPC eluting with chloroform, followed by recrystallization from chloroform to give 129 mg (0.348 mmol, 27% yield) of **PTzCO₂Et** as a yellow powder: M.p.: 221-222 °C. ¹H NMR (in CDCl₃): δ = 1.42 (3H, t, *J* = 6.8 Hz, CH₃), 4.41 (2H, q, *J* = 6.8 Hz, CH₂), 7.89 (1H, d, *J* = 4.0 Hz, thiophene), 8.62 (1H, d, *J* = 4.0 Hz, thiophene), 8.72 (1H, s, PTz). ¹³C NMR (in CDCl₃): δ = 14.3, 61.6, 110.0, 132.0, 134.2, 137.7, 145.7, 146.1, 146.6, 147.9, 156.4, 162.1. HR-MS (APCI) Calcd for C₁₂H₈BrN₃O₂S₂:

[M+H]⁺: 369.93141, Found: 369.93234.

Synthesis of 7-Bromo-4-[5-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-2-thieryl]-[1,2,5]thiadiazolo[3,4-c]pyridine (a-4)

A mixture of 146 mg (0.496 mmol) of **PTzBr2**, 176 mg (0.519 mmol) of **a-3**, 30.9 mg (5 mol%) of Pd(PPh₃)₄, 1.0 mL of 1M Na₂CO₃ aq, and 10 mL of THF was heated at 70 °C overnight with stirring. After usual workup using chloroform for extraction, the residue was subjected to silica gel chromatography eluting with hexane/ethyl acetate = 3/1 to give 123 mg (0.288 mmol, 58% yield) of **a-4** as a yellow powder: M.p.: 127-130 °C. ¹H NMR (in CDCl₃): δ = 1.33 (6H, s, CH₃), 1.36 (6H, s, CH₃), 6.22 (1H, s, CH), 7.28 (1H, d, *J* = 4.0 Hz, thiophene), 8.59 (1H, d, *J* = 4.0 Hz, thiophene), 8.66 (1H, s, PTz). ¹³C NMR (in CDCl₃): δ = 22.1, 24.2, 83.4, 96.6, 108.4, 127.6, 132.5, 141.1, 145.7, 147.5, 147.9, 149.8, 156.3. HR-MS (APCI) Calcd for C₁₆H₁₆BrN₃O₂S₂: [M+H]⁺: 425.99401, Found: 425.99429.

Synthesis of 5-(7-Bromo-[1,2,5]thiadiazolo[3,4-c]4-pyridyl)thiophene-2-carbaldehyde (PTzCHO)

A powder of 123 mg (0.288 mmol) of **a-4** was dissolved in 7 mL of 10% HCl aq and 13 mL of THF and the mixture was heated to reflux overnight with stirring. After usual workup using chloroform for extraction, the residue was subjected to silica gel chromatography eluting with hexane/ethyl acetate = 5/1 to give 83.5 mg (0.256 mmol, 89% yield) of **PTzCHO** as a yellow powder: M.p.: 209-211 °C. ¹H NMR (in CDCl₃): δ = 7.88 (1H, d, *J* = 4.0 Hz, thiophene), 8.73 (1H, d, *J* = 4.0 Hz, thiophene), 8.76 (1H, s, PTz), 10.02 (1H, s, formyl). ¹³C NMR (in CDCl₃): δ = 110.8, 132.2, 136.6, 145.8, 146.2, 146.3, 147.9, 148.8, 156.4, 183.4. HR-MS (APCI) Calcd for C₁₀H₄BrN₃OS₂: [M+H]⁺: 325.90519, Found: 325.90561.

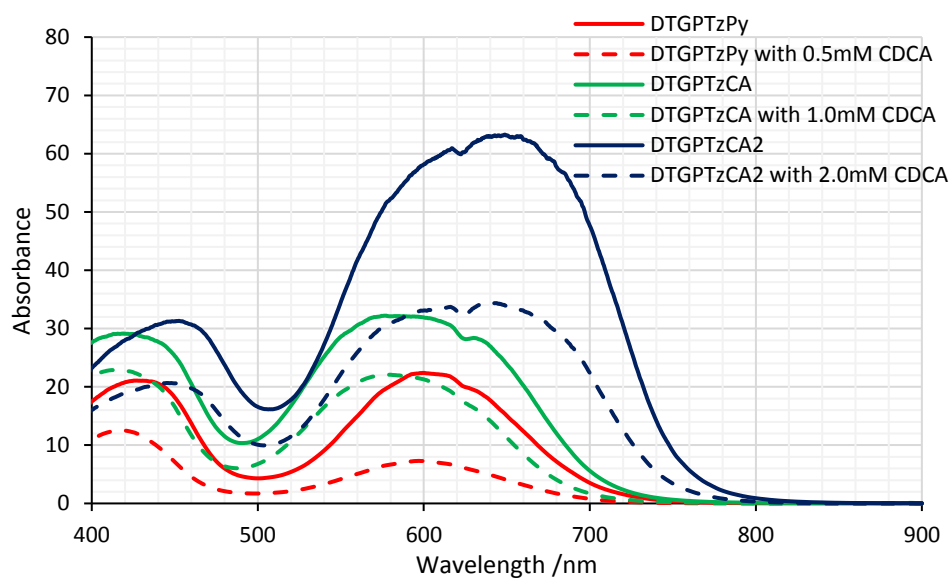


Figure S2 Absorption spectra of DTG-containing dyes on TiO₂ films.

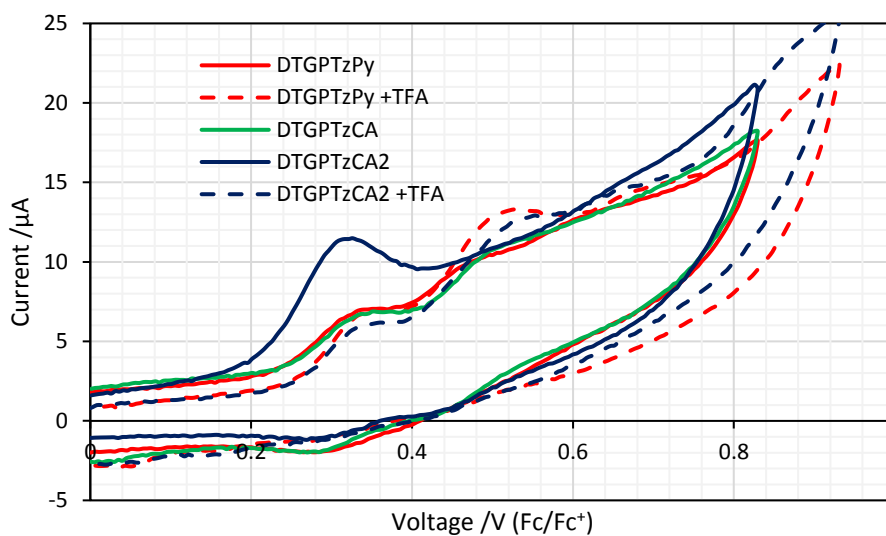


Figure S3 Cyclic voltammograms (first cycle) of the DTG-containing dyes.

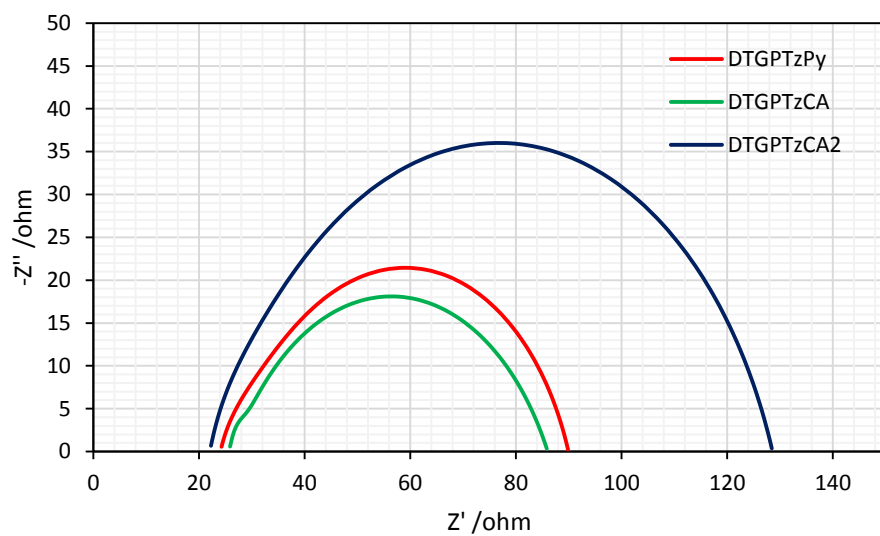


Figure S4 EIS Nyquist plots of DSSCs based on DTG-containing dyes.

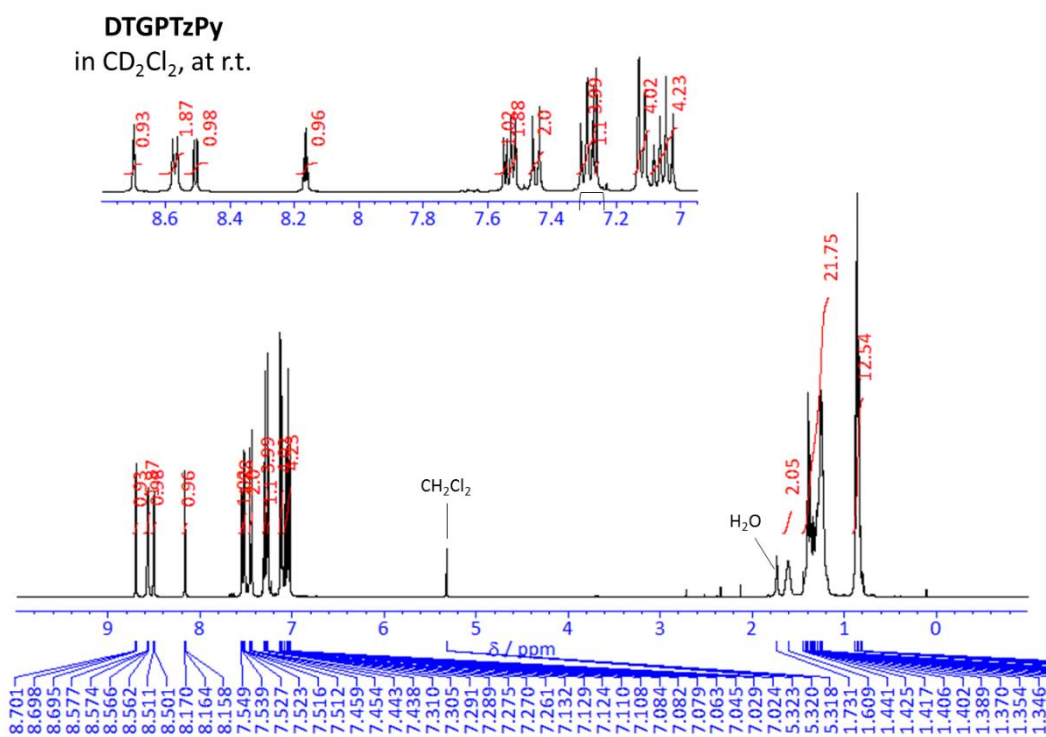


Figure S5 ^1H NMR spectrum of DTGPTzPy in CD_2Cl_2 .

DTGPTzCA
in CD₂Cl₂, at r.t.

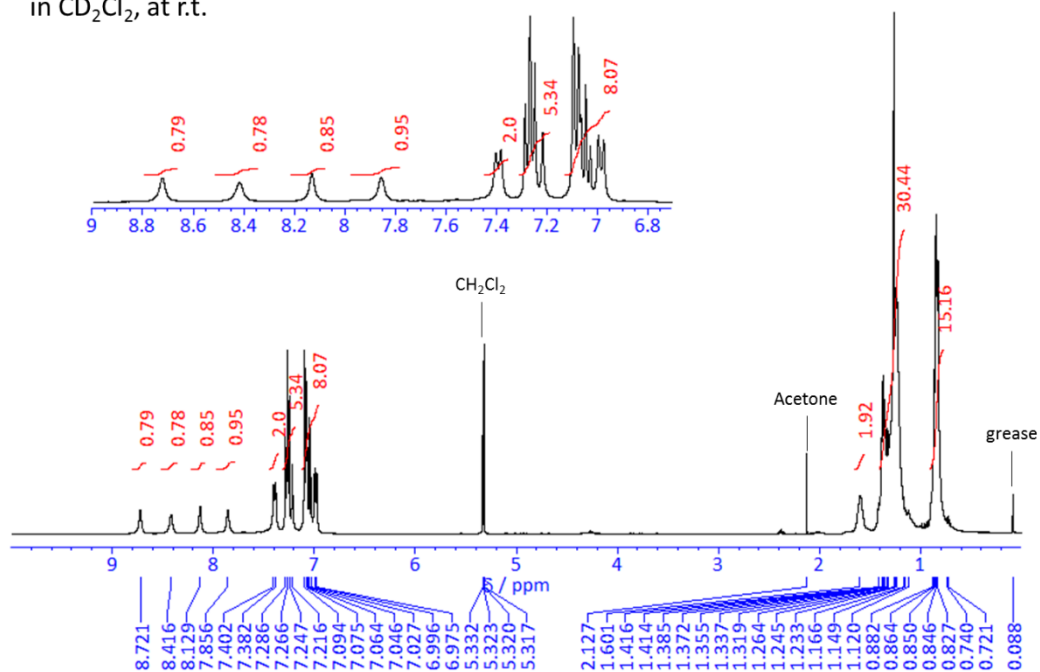


Figure S6 ¹H NMR spectrum of DTGPTzCA in CD₂Cl₂.

DTGPTzCA2
in DMSO-d₆, at r.t.

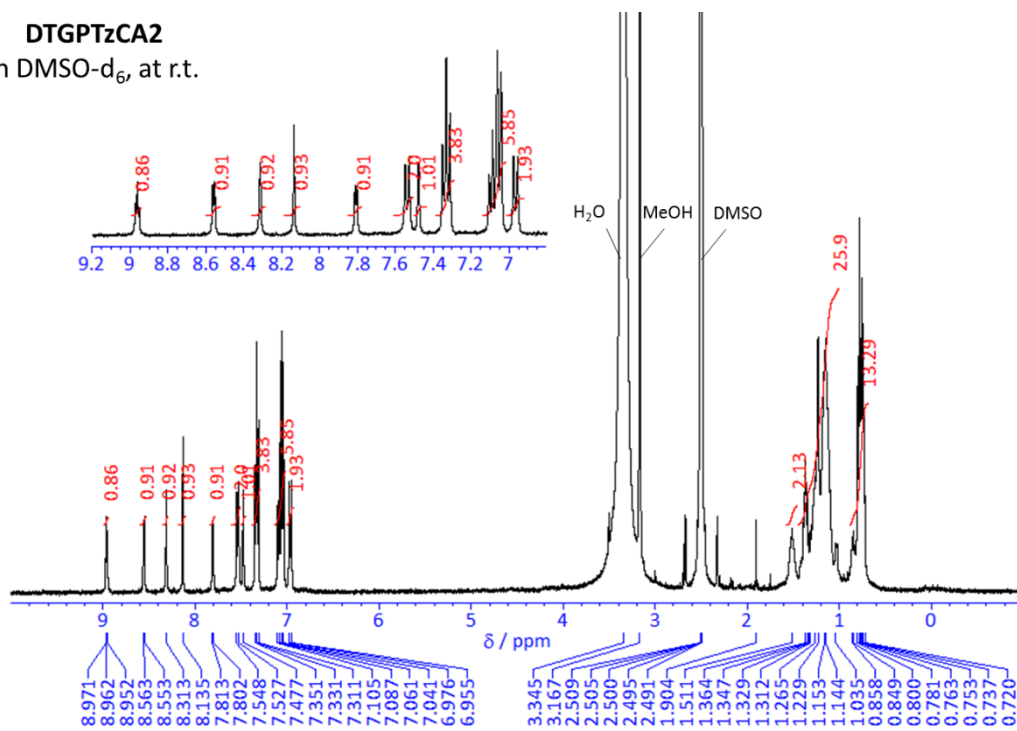


Figure S7 ¹H NMR spectrum of DTGPTzCA2 in DMSO-d₆.

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