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

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Supporting Information

Experimental

General

All reactions were carried out in dry argon. For the reaction solvents, diethyl ether, THF, DMF, toluene, and chlorobenzene were purchased from Kanto Chemical Co. Ltd. and were distilled from calcium hydride and stored over activated molecular sieves before use, whereas dichloromethane was distilled from calcium hydride immediately before use. Chloroform and acetic acid that were used as the reaction solvents for bromination with NBS were also purchased from Kanto chemical Co. Ltd. and used as obtained. Bis(trimethylsilyl)dibromobithiophene[1] and 2,5-bis(5-bromo-2-thienyl)-pyridine[2] were prepared according to the literature method. 1,2-Dichloro-tetra(*n*-hexyl)disilane was prepared in a fashion similar to what reported for 1,2-dichlorotetra(*n*-butyl)disilane.[3] The ^{1}H and ^{13}C NMR data obtained for 1,2-dichlorotetra(*n*-hexyl)disilane were consistent with those in the literature.[4] NMR spectra were recorded on a Varian System 500 spectrometer. IR spectra were recorded on a Shimadzu IRAffinity-1 spectrometer. UV-Vis spectra were measured with a Hitachi U-2910 spectrometer. Molecular weight of the present polymers were determined by gel permeation chromatography (GPC) using THF as an eluent and serially connected Shodex KF2001 and KF2002 columns, relative to the polystyrene standards. TGA was carried out on a SII TG/DTA-6200 analyzer under a gentle nitrogen flow (30 mL/min) at a heating rate of 10 ºC/min. Fabrication and evaluation of DSSCs were performed as reported in the literature.[4d] Usual workup for monomeric compounds mentioned below includes hydrolysis of the reaction mixture with water and separation of the organic layer. The aqueous layer was extracted with chloroform. The organic layer and the extract were combined and washed with water. After drying over anhydrous magnesium sulfate, the solvent was evaporated.

*Synthesis of **DSBTSi***

To a solution of 3.21 g (6.85 mmol) of 5,5'-bis(trimethylsilyl)-3,3'-dibromobithiophene in 70 mL of THF was added slowly 8.7 mL (13.7 mol) of a 1.58 M of *n*-butyllithium solution in hexane at -78°C over a period of 60 min. To this was added 3.25 g (6.95 mmol) of 1,2-dichlorotetra(*n*-hexyl)disilane at this temperature and the resulting mixture was stirred at room temperature overnight. After usual workup, the residue was subjected to silica gel column chromatography with hexane as an eluent to provide 3.45 g (4.89 mmol, 71% yield) of **DSBTSi** as a yellow oil. EI-MS: *m/z* = 704 [M^+]. ^{1}H NMR (in $CDCl_3$): δ = 0.32 (18H, s, CH_3Si), 0.76-0.93 (20H, m, *n*Hex), 1.16-1.37 (32H, m, *n*Hex), 7.12 (2H, s, thiophene). ^{13}C NMR (in $CDCl_3$): δ = 0.04, 12.90, 14.11, 22.56, 24.83, 31.45, 33.30, 133.85, 138.05, 140.30, 150.92. ^{29}Si NMR (in $CDCl_3$): δ = -6.90, -28.01. Anal. Calcd for $C_{38}H_{72}S_2Si_4$: C, 64.70; H, 10.29. Found: C, 64.70; H, 10.52.

Synthesis of ***DSBTBr***

To a solution of 1.11 g (1.57 mmol) of **DSBTSi** in 15 mL of dichloromethane was added 559 mg (3.14 mmol) of NBS in several portions and the mixture was stirred at room temperature for 3 h. After usual workup, the residue was subjected to silica gel column chromatography eluting with hexane to provide 0.983 g (1.37 mmol, 87% yield) of **DSBTBr** as a yellow oil. EI-MS: *m/z* = 716 [M^+ for ^{79}Br]. ^{1}H NMR (in $CDCl_3$): δ = 0.72-0.92 (20H, m, *n*Hex), 1.14-1.34 (32H, m, *n*Hex), 6.94 (2H, s, thiophene). ^{13}C NMR (in $CDCl_3$): δ = 12.65, 14.09, 22.58, 24.72, 31.39, 33.27, 110.10, 134.71, 135.62, 145.92. ^{29}Si NMR (in $CDCl_3$): δ = -27.80. Anal. Calcd for $C_{32}H_{54}Br_2S_2Si_2$: C, 53.47; H, 7.57. Found: C, 53.69; H, 7.58.

Synthesis of ***DSBTBrSn*** *and* ***DSBTSn***

To a solution of **DSBTBr** (691 mg, 0.962 mmol) in 15 mL of diethyl ether was added 0.61 mL of a 1.58 M *n*-butylithium in hexane at -78ºC over a period of 60 min. To this was added 212 mg (1.06 mmol) of trimethyltin chloride at this temperature and the

mixture was stirred at room temperature overnight. After usual workup, the residue was subjected to preparative GPC eluting with toluene to give 357 mg (0.445 mmol, 46% yield) of **DSBTBrSn** as a colorless oil. EI-MS: *m/z* = 802 [M^+]. ^{1}H NMR (in $CDCl_3$): δ = 0.39 (9H, s, CH_3Sn), 0.77-0.94 (20H, m, *n*Hex), 1.19-1.37 (32H, m, *n*Hex), 6.95 (1H, s, thiophene), 7.07 (1H, s, thiophene). ^{13}C NMR (in $CDCl_3$): δ = -8.10, 12.82, 12.86, 14.09 (2C), 22.57, 22.58, 24.77, 24.83, 31.43 (2C), 33.29, 33.32, 109.47, 133.60, 133.96, 135.53, 136.08, 141.29, 147.61, 150.15 (two sp^3 carbon signals may be overlapped with other signals). ^{29}Si NMR (in $CDCl_3$): δ = -28.02, -27.74. Anal. Calcd for $C_{35}H_{63}BrS_2Si_2Sn$: C, 52.37; H, 7.91. Found: C, 52.64; H, 8.03.

DSBTSn was prepared in a fashion similar to that above. Thus, treatment of **DSBTBr** with 2 equiv of *n*-BuLi then 2 equiv of trimethyltin chloride, followed by usual workup and purification of the residue by GPC gave **DSBTSn** (64% yield) as a colorless oil. EI-MS *m/z* = 886 [M^+ for ^{79}Br]. ^{1}H NMR (in $CDCl_3$): δ = 0.37 (18H, s, MeSn) 0.76-0.94 (20H, m, *n*Hex), 1.15-1.38 (32H, m, *n*Hex), 7.08 (2H, s, thiophene). ^{13}C NMR (in $CDCl_3$): δ = -8.12, 12.98, 14.11, 22.58, 24.86, 31.46, 33.33, 132.96, 135.26, 141.30, 151.61. ^{29}Si NMR (in $CDCl_3$): δ = -26.87. Anal. Calcd for $C_{38}H_{72}S_2Si_2Sn_2$: C, 51.47; H, 8.18. Found: C, 51.70; H, 8.24.

*Synthesis of **DSOBTBr***

From a 30 mL toluene solution of 440 mg (3.95 mmol) of trimethylamine N-oxide dihydrate ca. 10 mL of toluene was distilled to dry the solution azeotropically. To this was added 946 mg (1.32 mmol) of **DSBTBr** at room temperature and the mixture was heated to reflux for 2 h. After usual workup, the residue was subjected to silica gel column chromatography eluting with hexane to provide 858 mg (89% yield) of **DSOBTBr** as a yellow oil. EI-MS: *m/z* = 734 [M^+]. ^{1}H NMR (in $CDCl_3$): δ = 0.64-0.73 (8H, m, *n*Hex), 0.86 (12H, t, *J* = 7.2 Hz, CH3), 1.15-1.34 (32H, m, *n*Hex), 6.94 (2H, s, thiophene). ^{13}C NMR (in $CDCl_3$): δ = 14.13, 15.46, 22.53, 22.75, 31.47, 32.88, 112.33, 135.88, 139.59, 146.11. ^{29}Si NMR (in $CDCl_3$): δ = -1.48. Anal. Calcd

for $C_{32}H_{54}Br_2OS_2Si_2$: C, 52.30; H, 7.41. Found: C, 52.54; H, 7.45.

*Synthesis of **DSOBTBrSn***

Bromostannylsiloxane **DSOBTBrSn** was prepared from **DSOBTBr** in a fashion similar to that of **DSBTBrSn** in 56% yield as a yellow oil. EI-MS: *m/z* = 818 [M^+]. ^{1}H NMR (in $CDCl_3$): δ = 0.39 (9H, s, CH3Sn), 0.62-0.76 (8H, m, *n*Hex), 0.82-0.90 (12H, m, *n*Hex), 1.13-1.33 (32H, m, *n*Hex), 6.93 (1H, s, thiophene), 7.05 (1H, s, thiophene). ^{13}C NMR (in $CDCl_3$): δ = -8.10, 14.13, 14.15, 15.67, 15.74, 22.53 (2C), 22.77, 22.86, 31.49, 31.51, 32.91, 32.93, 111.35, 135.66, 138.15, 138.58, 138.95, 141.36, 147.86, 150.46. ^{29}Si NMR (in $CDCl_3$): δ = -1.88, -0.64. Anal. Calcd for $C_{35}H_{63}BrOS_2Si_2Sn$: C, 51.34; H, 7.76. Found: C, 51.38; H, 7.90.

Synthesis of 2-(tributylstannyl)-4-(n-hexyl)thiophene and 2-(trimethyl-stannyl)-3-(n-hexyl)thiophene

The title compounds were prepared in a fashion similar to what reported for 2-tributylstannyl-4-(*i*-butyl)thiophene [5] and 2-trimethylstannyl-3-(*n*-decyl or dodecyl)thiophene [6], respectively. Data for 2-tributylstannyl-4-(*n*-hexyl)thiophene. EI-MS: *m/z* = 401 [M^+-Bu]. ^{1}H NMR (in $CDCl_3$): δ = 0.82-1.70 (38H, m, *n*Bu, *n*Hex), 2.64 (2H, t, *J* = 7.6 Hz, CH_2 on thiophene), 6.96 (1H, s, thiophene), 7.18 (1H, s, thiophene). Data for 2-(trimethylstannyl)-3-(*n*-hexyl)thiophene. EI-MS: *m/z* = 317 [M^+-Me]. ^{1}H NMR (in $CDCl_3$): δ = 0.37 (9H, m, CH_3 on Sn), 0.89 (3H, t, *J* = 6.8 Hz, CH_3), 1.25-1.40 (6H, m, *n*Hex), 1.52-1.63 (2H, m, *n*Hex), 2.62 (2H, t, *J* = 8.0 Hz, CH_2 on thiophene), 7.09 (1H, d, *J* = 4.4 Hz, thiophene), 7.53 (1H, d, *J* = 4.8 Hz, thiophene).

*Synthesis of **TPzT1** and **TPzT2***

A mixture of 1.12 g (4.72 mmol) of 2,5-dibromopyrazne, 7.2 g (purity 60% based on the ^{1}H NMR spectrum, 9.45 mmol) of 2-tributylstannyl-4-*n*-hexylthiophene, 167 mg

(5mol%) of $PdCl_2(PPh_3)_2$, and 65 mL of DMF was heated at 85 ºC for 3 days. After usual workup, the residue was subjected to silica gel column chromatography with chloroform as an eluent, followed by recrystallization from ethanol/toluene to give 1.53 g (79% yield) of **TPzT1** as a yellow plate crystal. Mp 96.9-100.6 ºC. EI-MS: *m/z* = 412 [M^+]. ^{1}H NMR (in $CDCl_3$): δ = 0.89 (6H, t, *J* = 7.2 Hz, CH_3), 1.28-1.40 (12H, m, CH_2), 1.66 (4H, quint, *J* = 7.4 Hz, CH_2), 2.65 (4H, t, *J* = 7.2 Hz, CH_2 on thiophene), 7.08 (2H, d, *J* = 1.2 Hz, thiophene), 7.55 (2H, d, *J* = 1.2 Hz, thiophene), 8.83 (2H, s, pyrazine). ^{13}C NMR (in $CDCl_3$): δ = 14.10, 22.61, 28.95, 30.40, 31.52, 31.65, 123.57, 126.77, 139.26, 140.62, 144.92, 145.84. Anal. Calcd for $C_{24}H_{32}N_2S_2$: C, 69.86; H, 7.82; N, 6.79. Found: C, 69.86; H, 7.77; N, 6.77.

TPzT2 was prepared as a light yellow powder in 46% yield in a fashion similar to that above, by heating a mixture of 2,5-dibromopyrazne and 2-trimethyl-stannyl-3-*n*-hexylthiophene in toluene with $Pd_2(dba)_3$ (3 mol%)/P(*o*-tol)$_3$ (12 mol%) as the catalyst at 100 ºC for 3 days. Mp 69.9-71.0 ºC. EI-MS: *m/z* = 412 [M^+]. ^{1}H NMR (in $CDCl_3$): δ = 0.88 (6H, t, *J* = 6.8 Hz, CH_3), 1.26-1.45 (12H, m, CH_2), 1.70 (4H, quint, *J* = 7.6 Hz, CH_2), 2.93 (4H, t, *J* = 7.6 Hz, CH_2 on thiophene), 7.03 (2H, d, *J* = 5.2 Hz, thiophene), 7.38 (2H, d, *J* = 5.2 Hz, thiophene), 8.82 (2H, s, pyrazine). ^{13}C NMR (in $CDCl_3$): δ = 14.07, 22.59, 29.26, 29.88, 30.54, 31.65, 127.02, 131.06, 134.48, 141.39, 142.29, 146.37.

*Synthesis of **TPzT1Br** and **TPzT2Br***

To a solution of 301 mg (0.73 mmol) of **TPzT1** in a mixed solvent of 8 mL of acetic acid and 12 mL of chloroform was added 264 mg (1.48 mmol) of NBS in several portions. After usual workup, the residue was subjected to silica gel column chromatography with chloroform as the eluent to give 338 mg (0.59 mmol, 81% yield) of **TPzT1Br** as a yellow needle crystal. Mp 118.2-123.0 ºC. EI-MS: *m/z* = 568 [M^+ for ^{79}Br]. ^{1}H NMR (in $CDCl_3$): δ = 0.90 (6H, t, *J* = 7.2 Hz, CH_3), 1.27-1.42 (12H, m,

CH_2), 1.63 (4H, quint, J = 7.6 Hz, CH_2), 2.59 (4H, t, J = 7.6 Hz, CH_2 on thiophene), 7.35 (2H, s, thiophene), 8.73 (2H, s, pyrazine). ^{13}C NMR (in $CDCl_3$): δ = 14.09, 22.58, 28.88, 29.64, 29.68, 31.59, 113.37, 126.02, 138.78, 140.52, 143.80, 145.28. Anal. Calcd for $C_{24}H_{30}Br_2N_2S_2$: C, 50.53; H, 5.30; N, 4.91. Found: C, 50.58; H, 5.10; N, 4.89

TPzT2Br was prepared in a fashion similar to that above and purified by GPC with chloroform as the eluent, followed by recrystallization from ethanol as an orange needle crystal in 43% yield. Mp 98.5-104.8 ºC. EI-MS: *m/z* = 568 [M^+ for ^{79}Br]. ^{1}H NMR (in $CDCl_3$): δ = 0.89 (6H, t, J = 7.2 Hz, CH_3), 1.26-1.44 (12H, m, CH_2), 1.67 (4H, quint, J = 7.6 Hz, CH_2), 2.86 (4H, t, J = 7.6 Hz, CH_2 on thiophene), 6.97 (2H, s, thiophene), 8.71 (2H, s, pyrazine). ^{13}C NMR (in $CDCl_3$): δ = 14.06, 22.55, 29.17, 29.98, 30.27, 31.59, 115.10, 133.79, 136.30, 140.78, 142.84, 145.57. Anal. Calcd for $C_{24}H_{30}Br_2N_2S_2$: C, 50.53; H, 5.30; N, 4.91; S, 11.24. Found: C, 50.77; H, 5.34; N, 4.87; S, 11.52.

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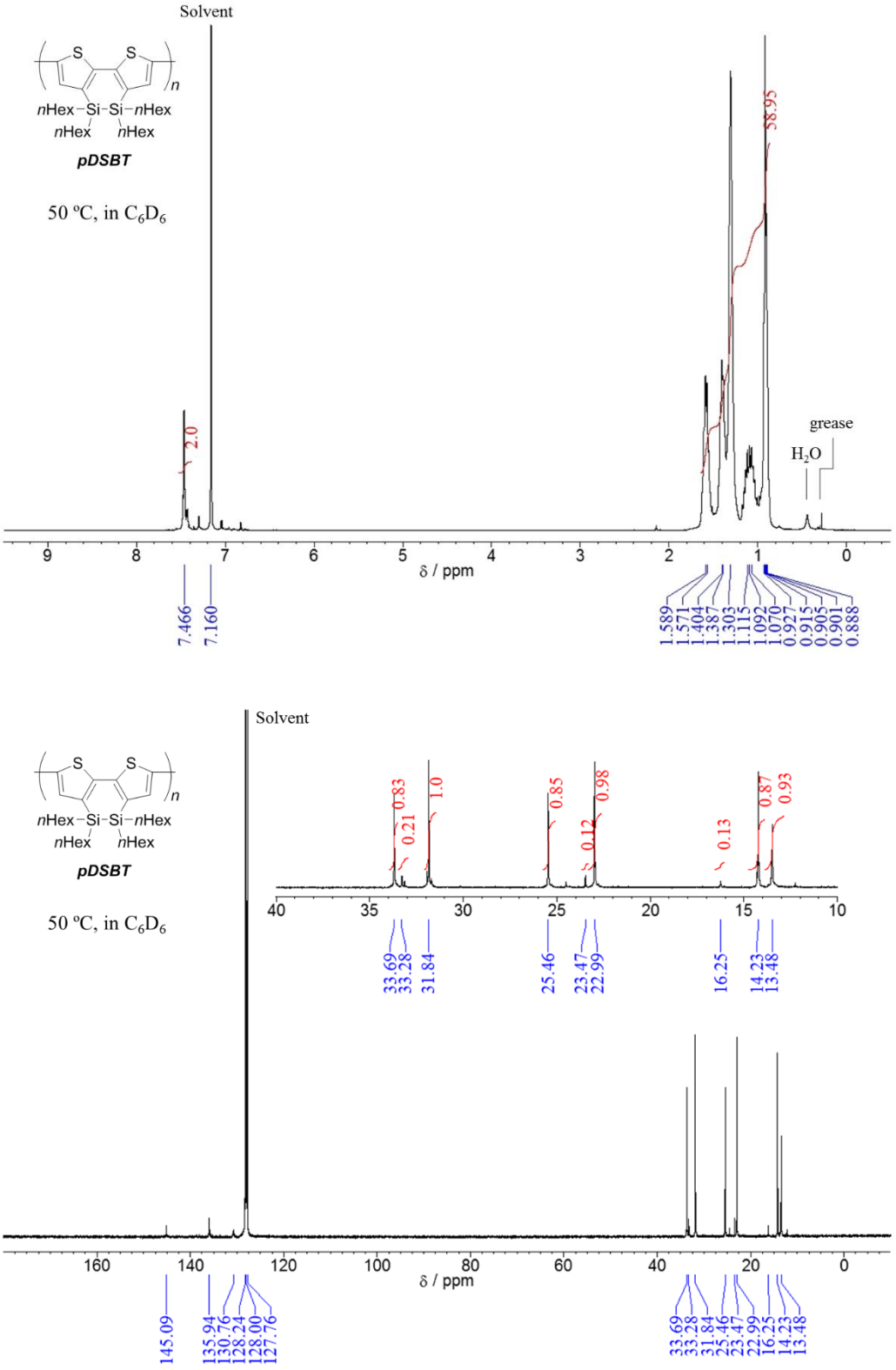

Figure S-1. NMR spectra of DSBT-containing polymers.

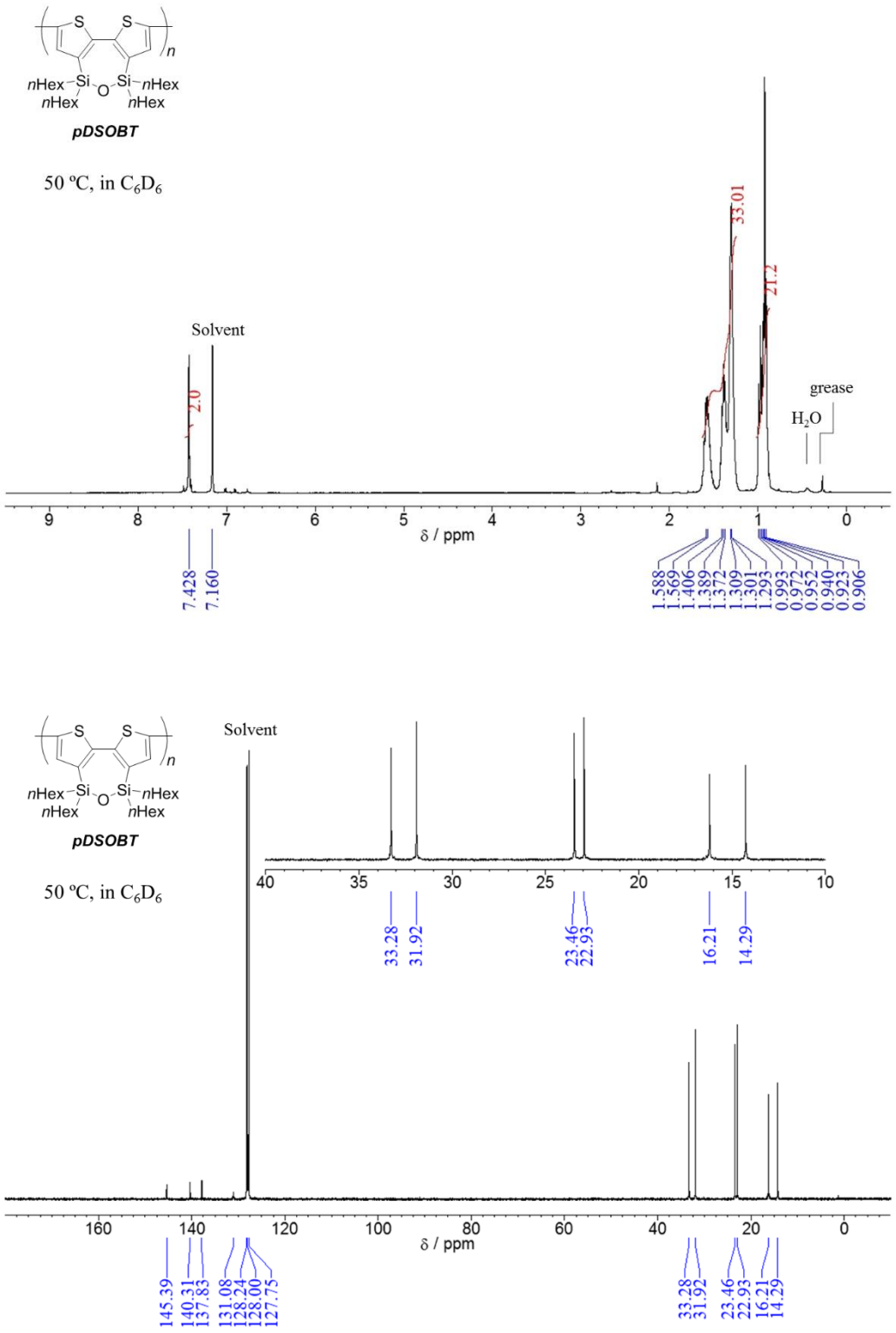

Figure S-1. NMR spectra of DSBT-containing polymers (continued).

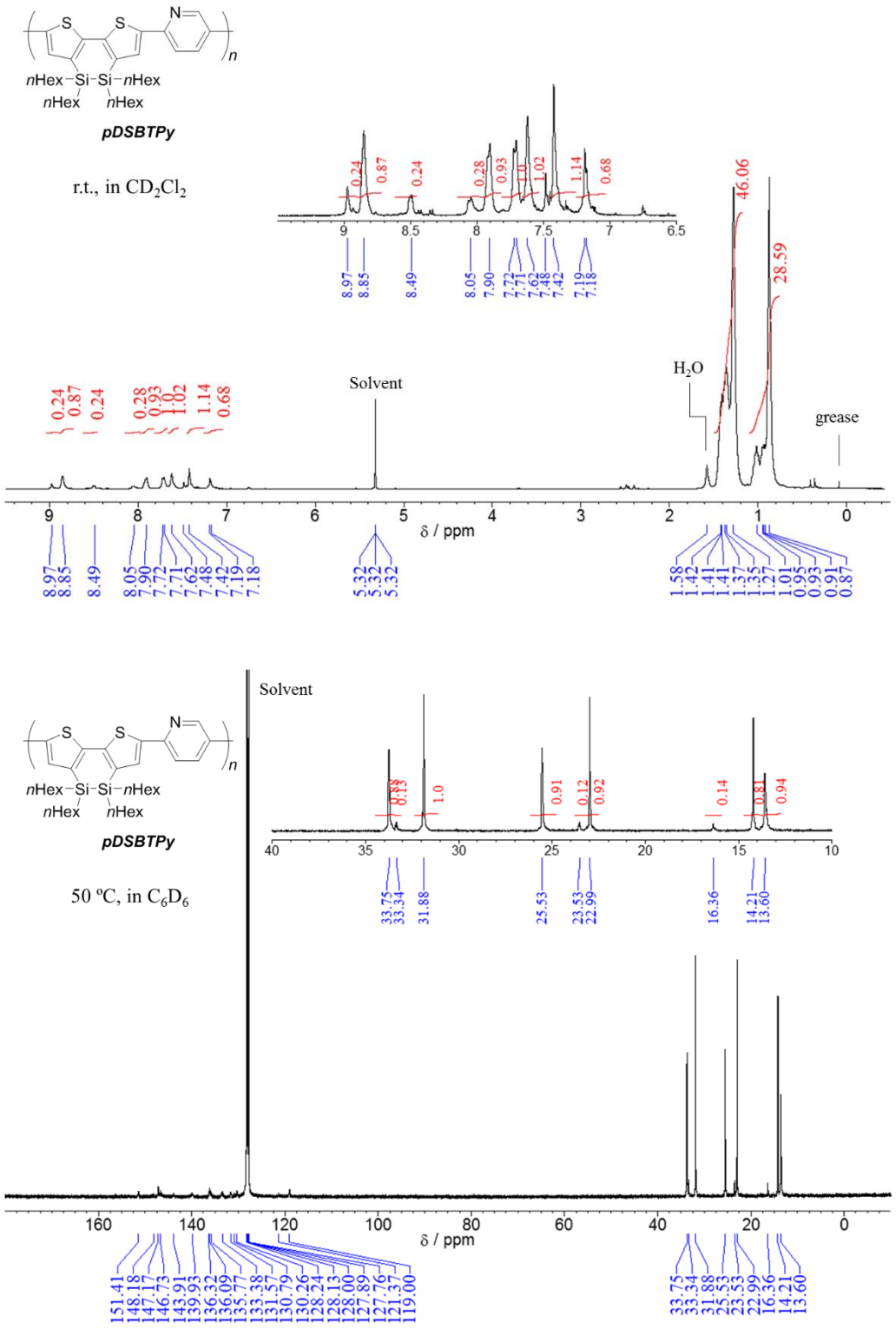

Figure S-1. NMR spectra of DSBT-containing polymers (continued).

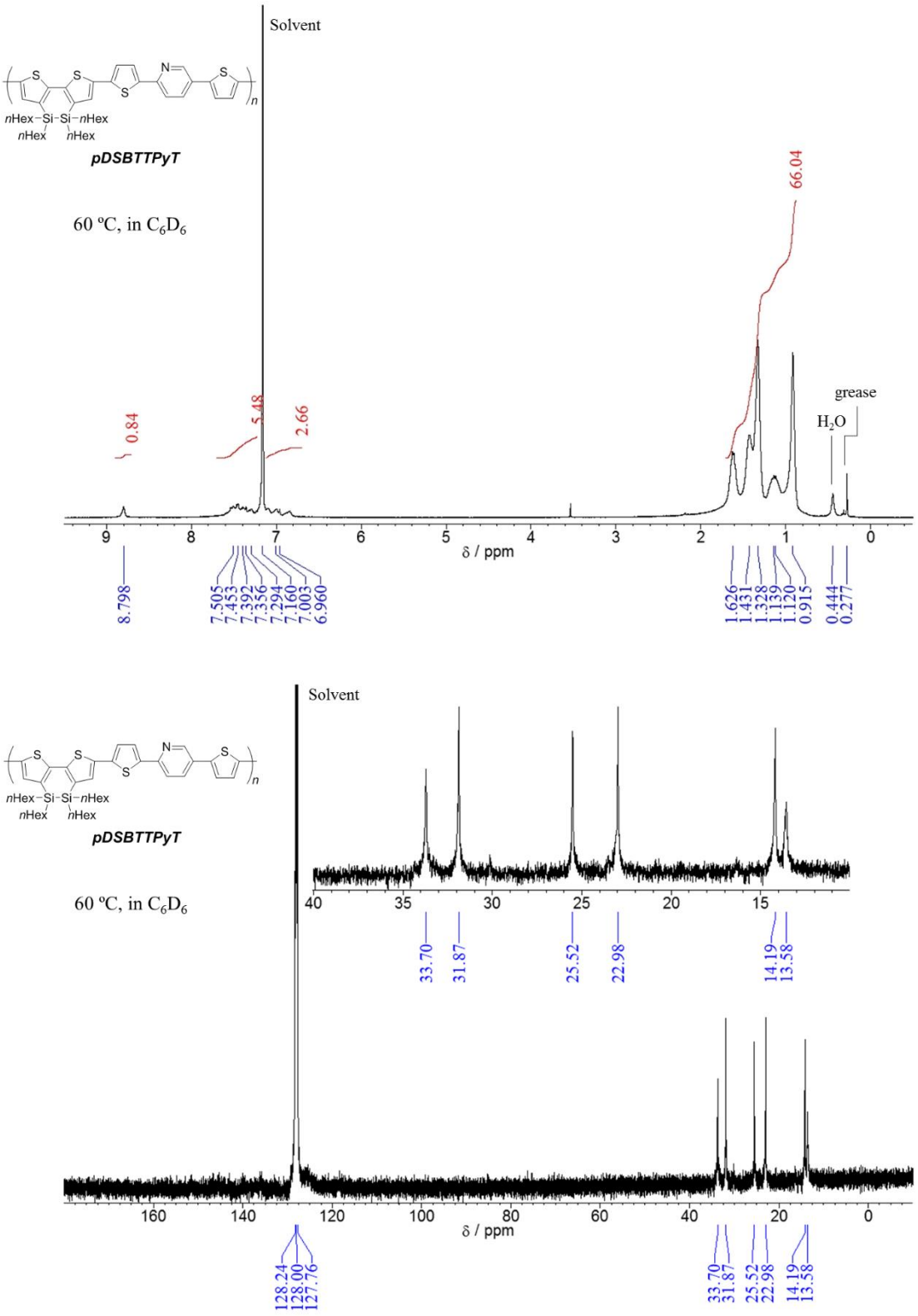

Figure S-1. NMR spectra of DSBT-containing polymers (continued).

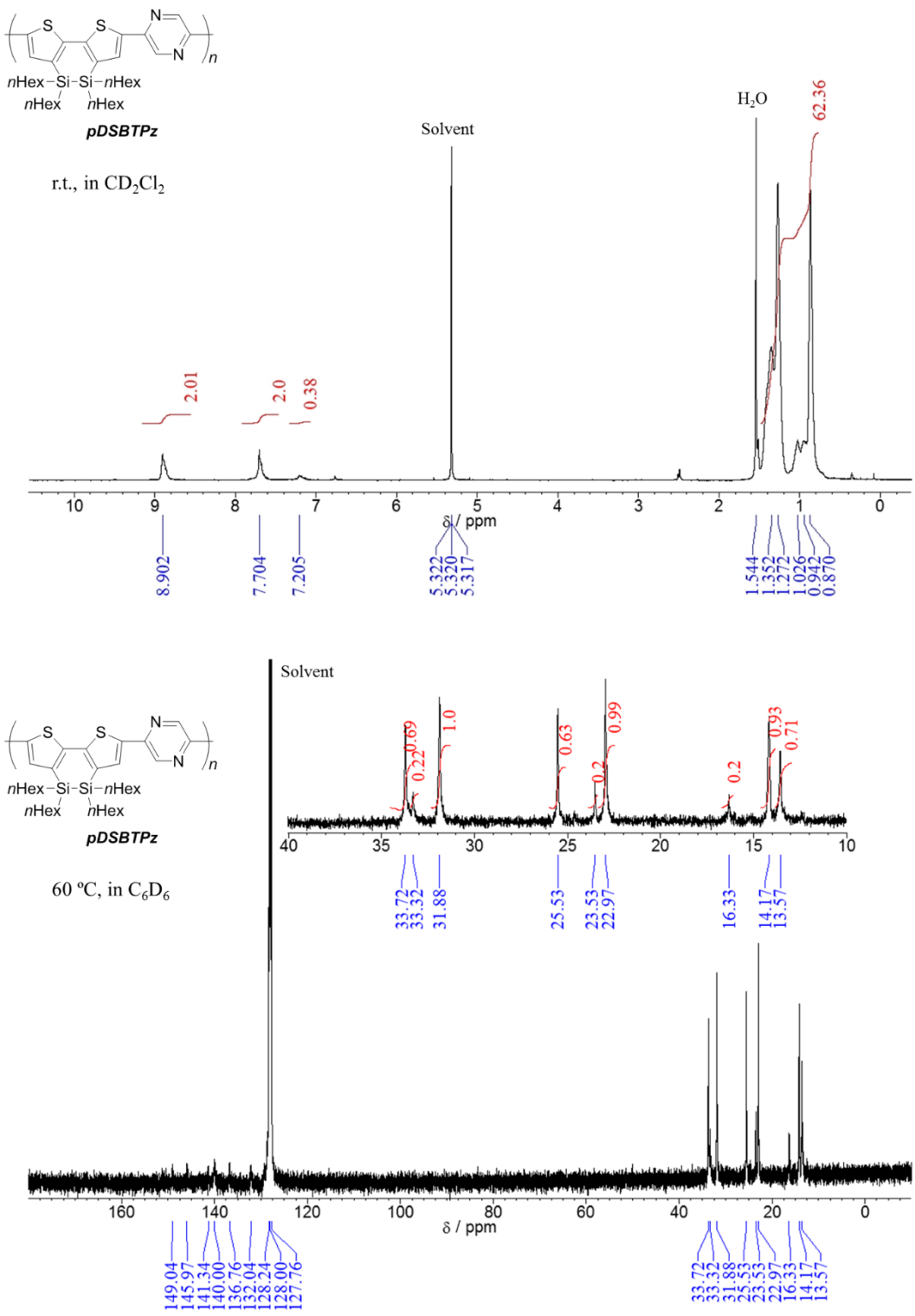

Figure S-1. NMR spectra of DSBT-containing polymers (continued).

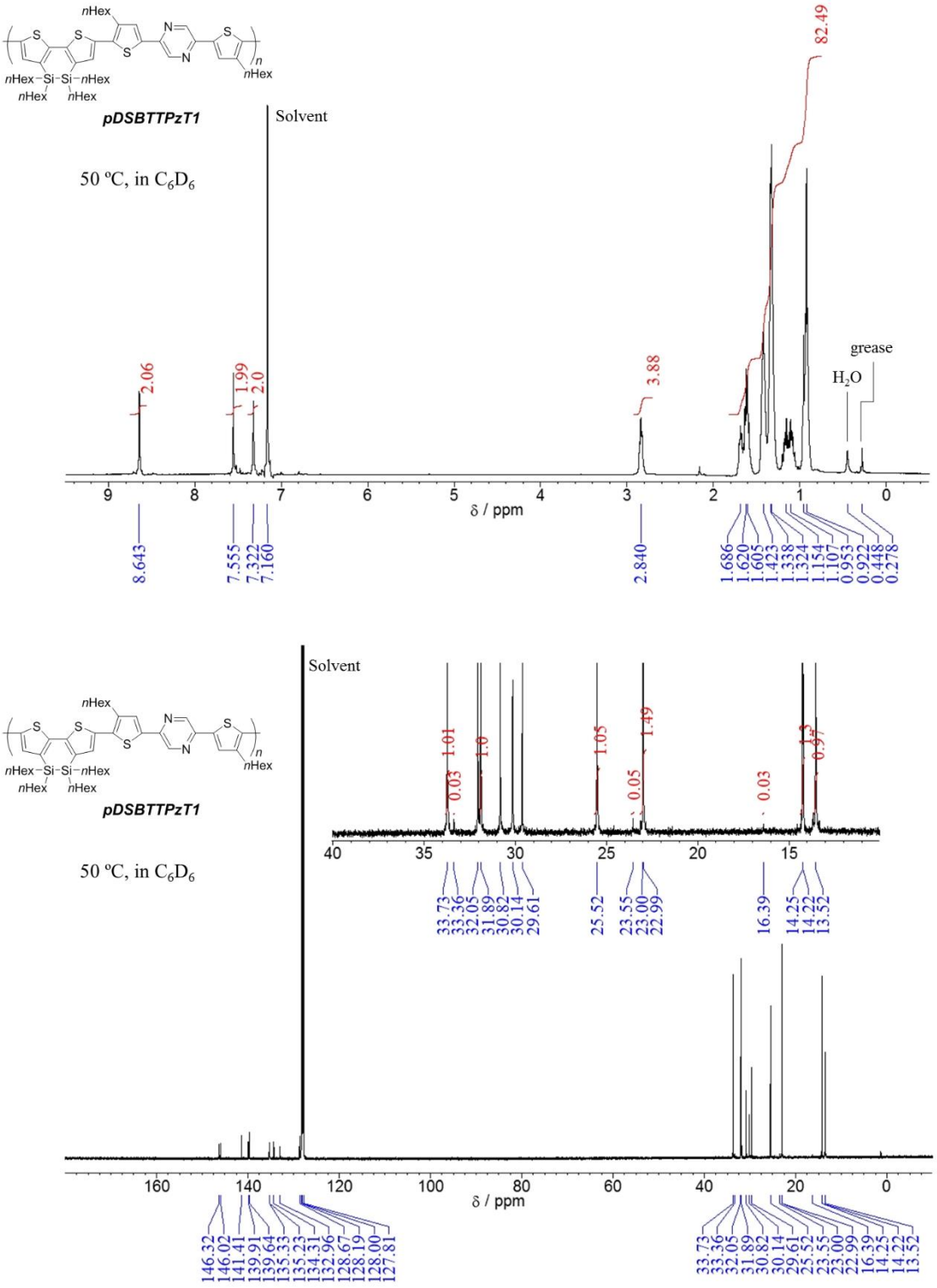

Figure S-1. NMR spectra of DSBT-containing polymers (continued).

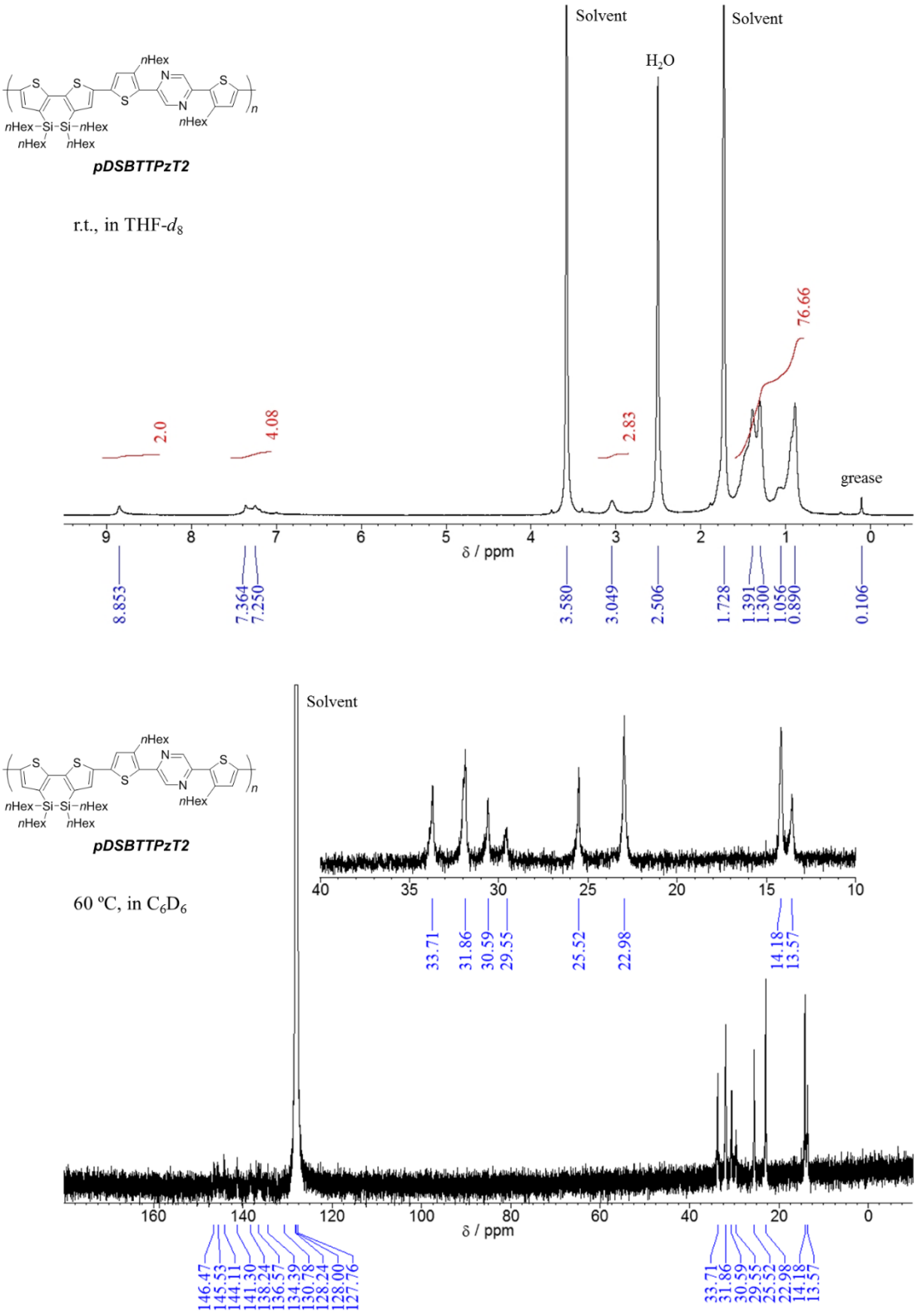

Figure S-1. NMR spectra of DSBT-containing polymers (continued).

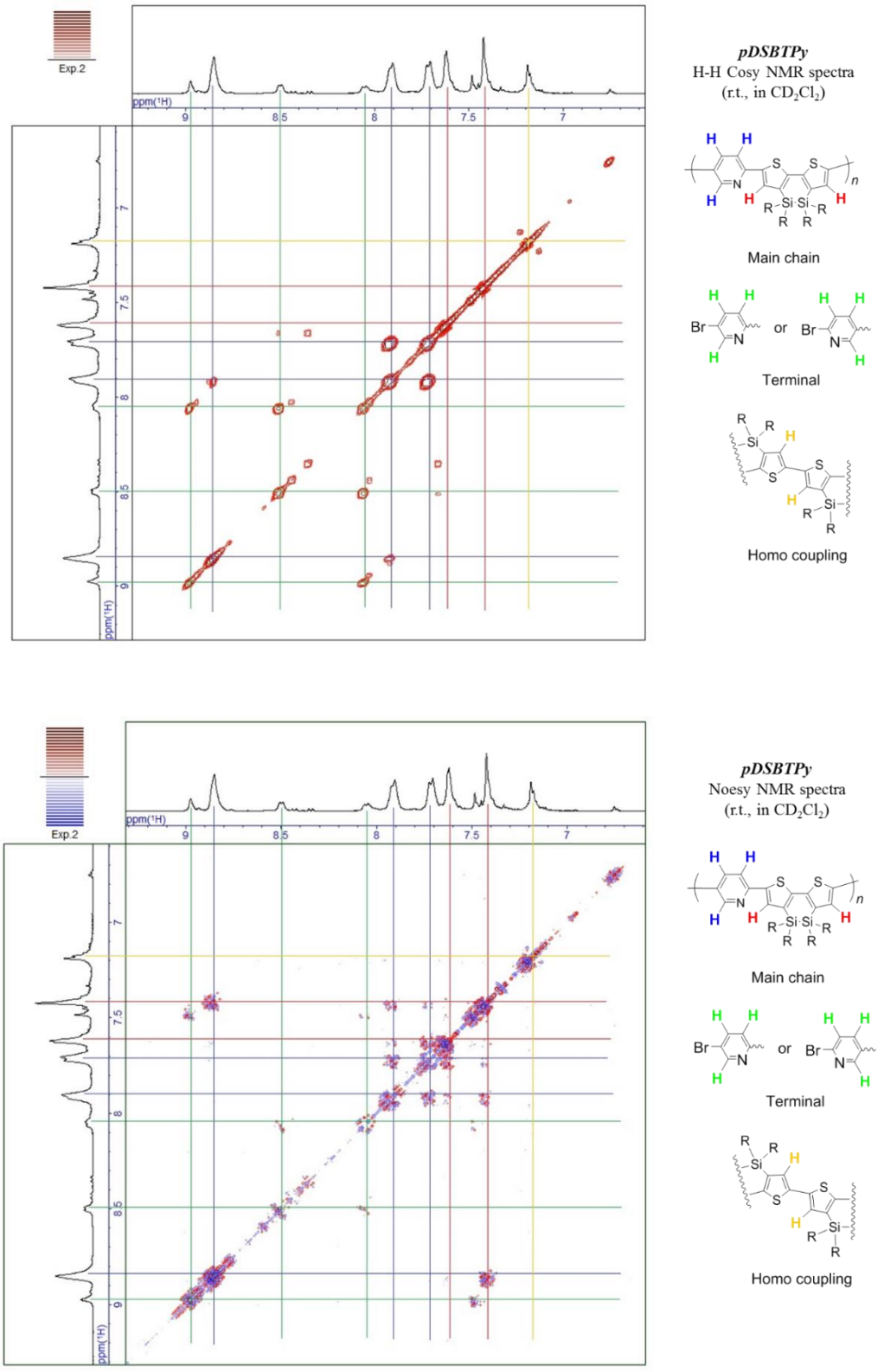

Figure S-1. NMR spectra of DSBT-containing polymers (continued).

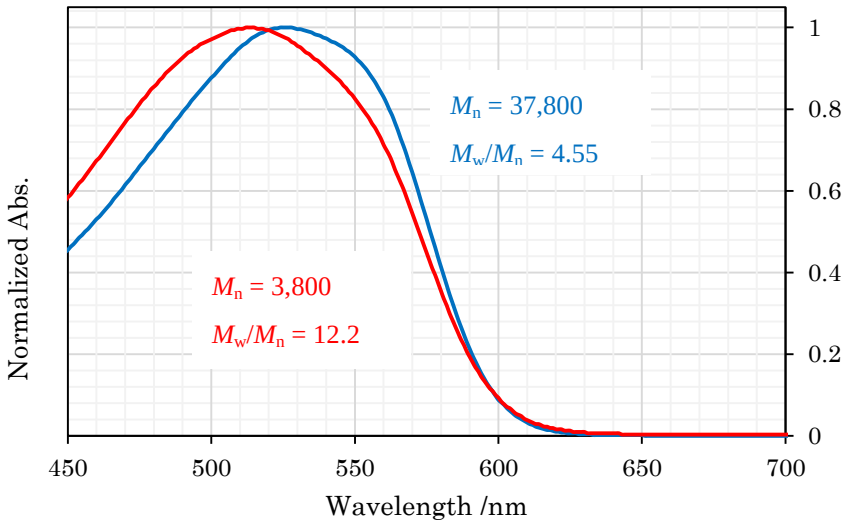

Figure S-2. Molecular weight-dependence of absorption spectra of **pDSBTTPzT2**.