Supplementary Information

Oligo(ethylene glycol) Side Chain Effect on the Physical Property and Molecular Arrangement of Oligothiophene-Isoindigo Based Conjugated Polymers

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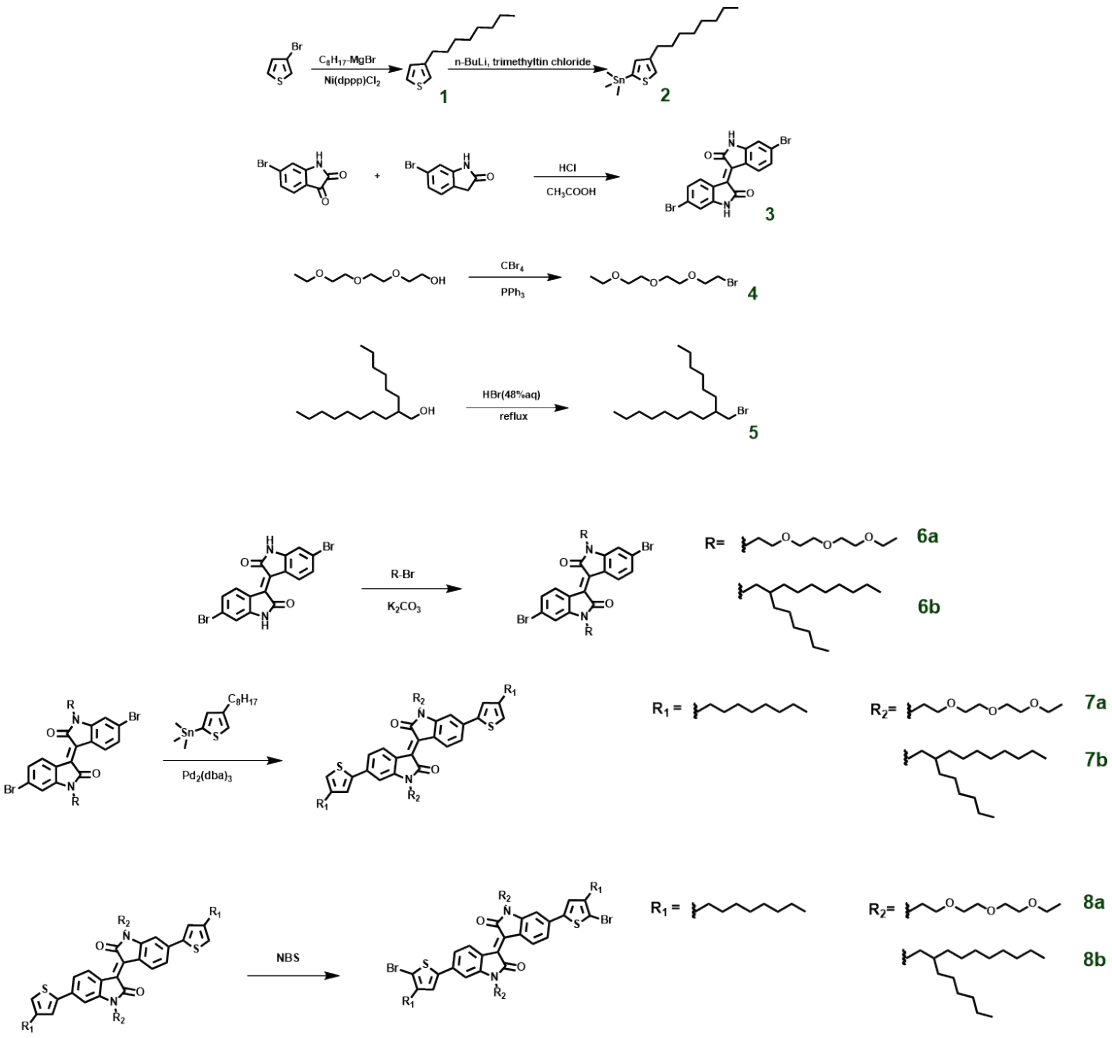
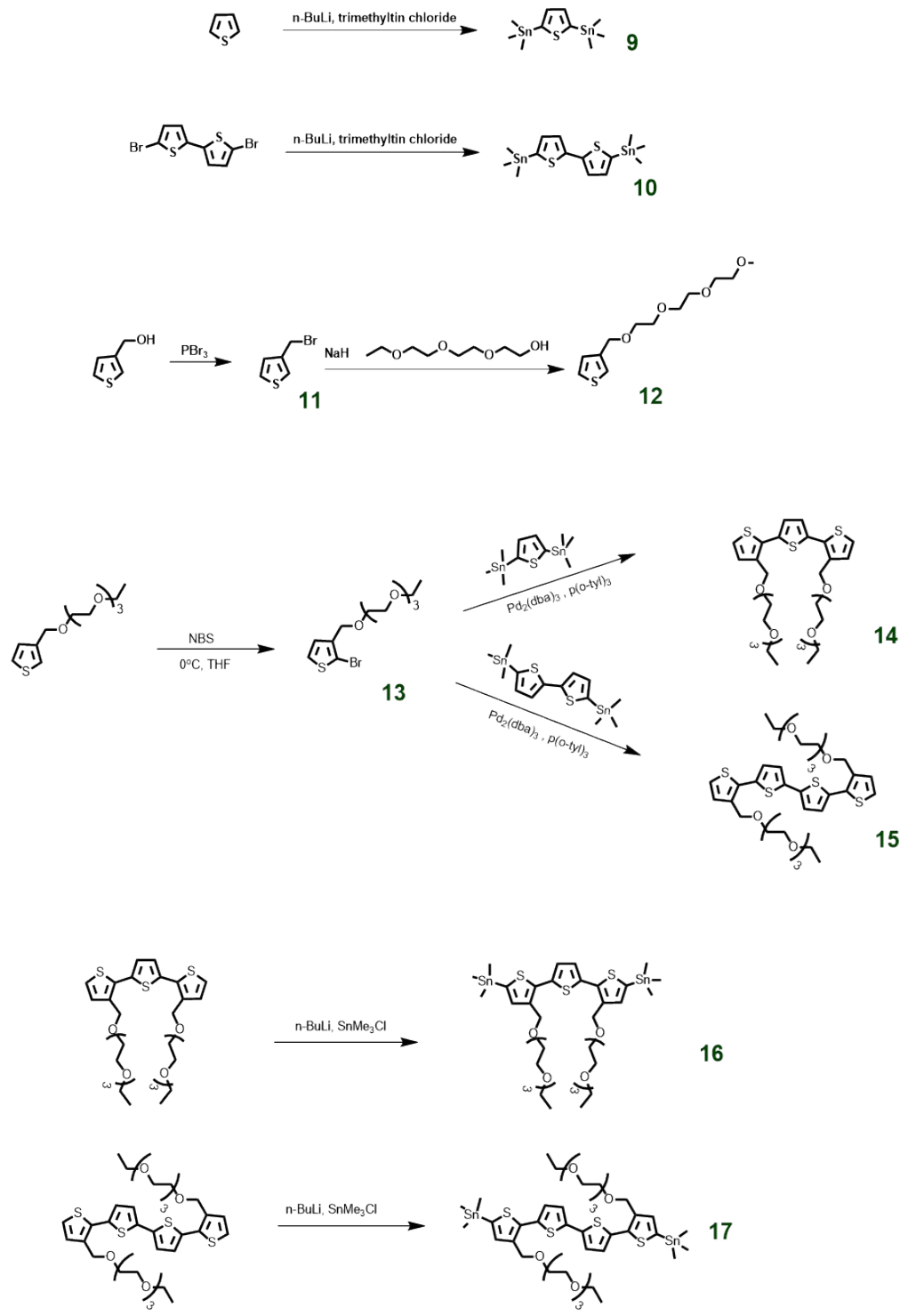
1. Synthesis of the Monomers and the Polymers

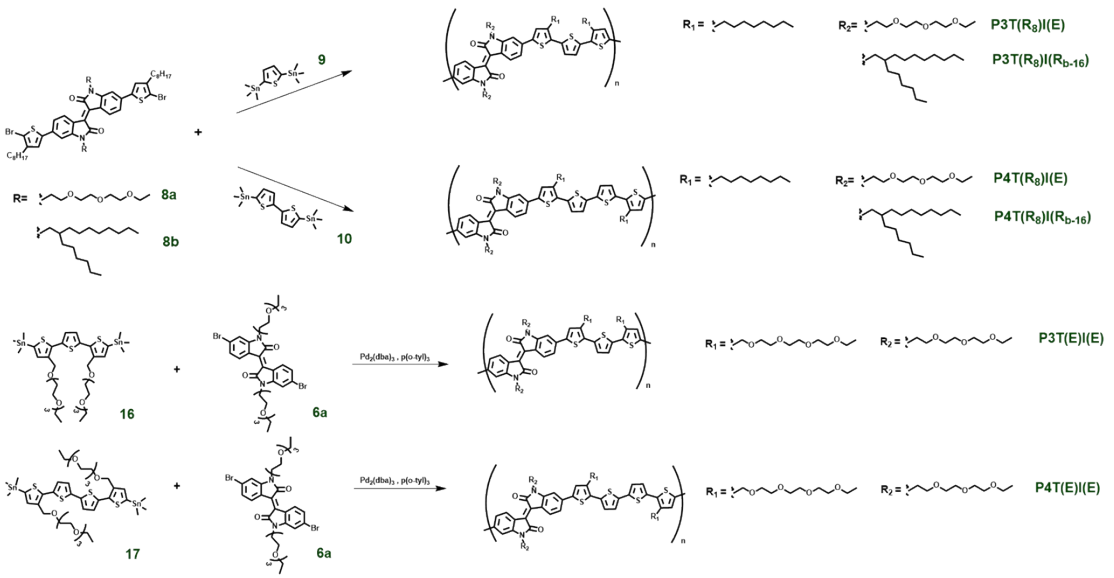
Scheme S1.1, S1.2, and S1.3 show the synthesis scheme of all intermediates and polymers. All reagents purchased from Acros and Aldrich with purity >99%, they were used as received.



Scheme S1.1. Synthesis scheme of compound 1 ~ compound 8



Scheme S1.2. Synthesis scheme of compound 9 ~ compound 17



Scheme S1.3. Synthesis scheme of P3TI and P4TI polymers

Synthesis of compound 1

3-octylthiophene

A 500 ml round bottom flask (flask A) and a 1000 ml round bottom flask (flask B) were evacuated by vacuum system and refilled the nitrogen to remove the moisture in the flask. Then, magnesium (8.95 g, 0.37 mole) and 300 ml anhydrous ether were placed in the flask A, and 3-bromothiophene (30.00 g, 0.18 mole), [1,3-Bis(diphenylphosphino)propane]dichloronickel(II) (200 mg, 0.37 mmole), and 300 ml anhydrous ether were placed in the flask B. Then the flask A was put in 0 ^{o}C ice bath and 1-bromooctane (53.30 g, 0.28 mole) was added into the flask A through syringe slowly in 2 hours. After complete adding 1-bromooctane, the mixture was stirred under room temperature for 2 hours. Then, the solution in the flask A was transferred in the flask B. After that, the mixture was stirred under room temperature for 10 hours. Then, 200 ml 1M hydrochloric acid was added into the flask B to terminate the reaction and the solution was extracted by using ether and distilled water. The organic layer was collected, dried over anhydrous magnesium sulfate, and filtered by filter paper. The filtrate was collected and the ether was removed by rotary evaporator. Finally, the condensed mixture can be further purified by distillation under reduced pressure (60 ^{o}C, 0.08 torr) to obtain colorless oil, compound 15 (28.54 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, J = 4.9, 2.9 Hz, 1H), 6.93 (dd, J = 6.6, 3.9 Hz, 2H), 2.62 (t, J = 7.8 Hz, 2H), 1.68 – 1.57 (m, 2H), 1.35 – 1.22 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H).

Synthesis of compound 2

trimethyl(4-octylthiophene-2-yl)stannane

A 150 ml round bottom flask was evacuated by vacuum system and refilled the nitrogen to remove the moisture in the flask. Next, compound 15 (4.91 g, 25 mmole) and 50 ml anhydrous tetrahydrofuran were placed in the flask. After that, the flask was put in -78^{o}C dry ice bath. Then, 10 ml 2.5M n-butyllithium in hexane solution (25 mmole) was added into the flask and the solution was stirred for 2 hours. The -78^{o}C dry ice bath was removed and the solution was stirred at room temperature for 1 hour. Then the flask was put in -78^{o}C dry ice bath again and 25 ml 1M trimethyltin chloride in tetrahydrofuran solution (25 mmole) was added into the flask. After complete adding the trimethyltin chloride solution, the -78^{o}C dry ice bath was removed and the solution was stirred at room temperature for 12 hours. The mixture was extracted by hexane and distilled water. The organic layer was collected, dried over anhydrous magnesium sulfate, and filtered by filter paper. The filtrate was collected and the hexane was removed by rotary evaporator. Finally, the condensed mixture can be further purified by column chromatography (hexane as eluent, celite gel) to obtain pale yellow oil, compound 16 (7.03 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 0.8 Hz, 1H), 7.01 (s, 1H), 2.65 (t, *J* = 7.8 Hz, 2H), 1.63 (quintet, *J* = 7.5 Hz, 2H), 1.29 (d, *J* = 21.8 Hz, 10H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.35 (s, 9H).

Synthesis of compound 3

(E)-6,6'-dibromo-[3,3'-biindolinylidene]-2,2'-dione

6-bromooxindole (23.45g, 0.11mole), 6-bromoisatin (25.00g, 0.11mole), 750 ml acetic acid, and 5 ml hydrochloric acid were placed in a 1000 ml flask. The mixture was heated to reflux for 24 hours. Then the mixture was filtered by filter paper and washed by methanol several times until the filtrate was neutral. Finally, the solid was collected and dried to obtain dark red solid, compound 17 (45.53g, 98%). ^{1}H NMR (400MHz, D_6-DMSO) δ 11.11(s, 2H), 9.03(d, *J*=8.6Hz, 2H), 7.22(d, *J*=8.7Hz, 2H), 7.03(s, 2H)

Synthesis of compound 4

1-bromo-2-(2-(2-ethoxyethoxy)ethoxy)ethane

2-(2-(2-ethoxyethoxy)ethoxy)ethanol (10.00 g, 56.11 mmole) and tetrabromomethane (24.19 g, 72.94 mmole) were dissolved in 100 ml of anhydrous dichloromethane and then the solution was cooled to 0℃ in ice bath. A solution of triphenylphosphine (17.66 g, 67.33 mmole) in 100 ml of anhydrous dichloromethane was slowly transferred into the aforementioned low temperature solution. After the transfer was finished, ice bath was removed and the solution was reacted at ambient temperature

under stirring for 20 hours. Then, the dichloromethane was removed by rotary evaporator. The sticky yellow solid was obtained and it was washed several times by ether. The combined ether solution was concentrated, and then distilled under vacuum (100 ^{o}C, 0.08 torr) to obtain colorless oil, compound 18 (11.21 g, 83 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (t, *J* = 6.4 Hz, 2H), 3.70 – 3.63 (m, 6H), 3.59 (m, 2H), 3.52 (q, *J* = 7.0 Hz, 2H), 3.47 (t, *J* = 6.4 Hz, 2H), 1.21 (t, *J* = 7.0 Hz, 3H).

Synthesis of compound 5

7-(bromomethyl)pentadecane

2-hexyl-1-decanol (40.00 g, 0.17 mole) and 48wt% hydrogen bromide aqueous solution (100.00 g, 0.49 mole) were placed in a 250 ml flask. The mixture was heated to reflux for 10 hours. The mixture was extracted by hexane and distilled water. The organic layer was collected, dried over anhydrous magnesium sulfate, and filtered by filter paper. The filtrate was collected and the hexane was removed by rotary evaporator. The condensed mixture was further purified by column chromatography (toluene as eluent) to obtain colorless oil, compound 19 (47.86g, 95%). ^{1}H NMR (400MHz, $CDCl_3$) δ 3.45(d, *J*=4.8Hz, 2H), 1.63-1.55(m, 1H), 1.45-1.17(m, 24H), 0.93-0.81(m, 6H)

Synthesis of compound 6a

(E)-6,6'-dibromo-1,1'-bis(2-(2-(2-ethoxyethoxy)ethoxy)ethyl)-[3,3'-biindolinylidene]-2,2'-dione

Compound 17 (5.00 g, 11.90 mmole), compound 18 (6.76 g, 29.76 mmole) and anhydrous potassium carbonate (8.22 g, 59.5 mmole) were placed in a round bottom flask. 100 ml of anhydrous dimethylformamide was added and the mixture was reacted at 90 ^{o}C for 12 hours under stirring. After the solution was cooled to ambient temperature, the mixture was extracted with ether and distilled water several times. The combined organic layers were dried over anhydrous magnesium sulfate and the solution was filtered. Ether was removed by rotary evaporator, and the solid product was purified by silica gel column chromatography with ether as eluent. After removal of ether, the product was recrystallized from cold hexane. The red solid was collected by filtration, compound 20a (8.28 g, 94%). ^{1}H NMR (400 MHz, acetone) δ 9.14 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 1.9 Hz, 2H), 7.19 (dd, J = 8.6, 1.9 Hz, 2H), 4.02 (t, J = 5.4 Hz, 4H), 3.78 (t, J = 5.4 Hz, 4H), 3.61 – 3.36 (m, 20H), 1.08 (t, J = 7.0 Hz, 6H).

Synthesis of compound 6b

(E)-6,6'-dibromo-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione

Compound 17 (5.00 g, 11.90 mmole), compound 19 (9.08 g, 29.76 mmole) and

anhydrous potassium carbonate (8.22 g, 59.5 mmole) were used to do the reaction. Following the synthetic procedure of compound 20a, (5.86 g, 77%), and the solid product was purified by silica gel column chromatography with solvent mixture hexane: dichloromethane = 2: 1 (v/v) as eluent. After removal of the solvents, the product was recrystallized from methanol. The reddish solid was collected by filtration, compound 20b (9.82 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 8.6 Hz, 2H), 7.15 (dd, *J* = 8.6, 1.8 Hz, 2H), 6.88 (d, *J* = 1.7 Hz, 2H), 3.61 (d, *J* = 7.5 Hz, 4H), 1.91-1.83 (m, 2H), 1.39 – 1.20 (m, 24H), 0.86 (m, *J* = 6.8 Hz, 6H).

Synthesis of compound 7a

(E)-1,1'-bis(2-(2-(2-ethoxyethoxy)ethoxy)ethyl)-6,6'-bis(4-octylthiophene-2-yl)-[3,3'-biindolinylidene]-2,2'-dione

Compound 20a (1.50 g, 2.03 mmole), compound 16 (2.19 g, 6.09 mmole), tris(dibenzylideneacetone)dipalladium(0) (92.7 mg, 0.10 mmole), and tri(o-tolyl)phosphine (61.8 mg , 0.20 mmole) were added to a 10 ml microwave tube. After being capped with Teflon septum, the tube was vacuumed and refilled with nitrogen three times. Anhydrous tetrahydrofurane (3 ml) was added to the tube via syringe. The parameter of microwave was set to be 90 ^{o}C, 100 W and 15 minutes under standard mode. After the tube was cooled down, the mixture was concentrated and then purified by silica gel column chromatography with ether as eluent. Ether was then removed under reduced pressure, and the residual sticky product was recrystallized in cold hexane to obtain dark red solid, compound 21a (1.79 g, 91 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, *J* = 8.4 Hz, 2H), 7.28 (dd, *J* = 4.2, 1.5 Hz, 3H), 7.25 (d, *J* = 1.9 Hz, 1H), 7.16 (d, *J* = 1.7 Hz, 2H), 6.94 (d, *J* = 1.1 Hz, 2H), 4.05 (t, *J* = 5.8 Hz, 4H), 3.79 (t, *J* = 5.7 Hz, 4H), 3.67 – 3.63 (m, 4H), 3.62 – 3.59 (m, 4H), 3.56 – 3.52 (m, 4H), 3.48 – 3.42 (m, 8H), 2.65 – 2.61 (m, 4H), 1.67 (quintet, *J* = 7.5 Hz,4H), 1.42 – 1.24 (m, 6H), 1.16 (t, *J* = 7.0 Hz, 6H), 0.89 (t, *J* = 6.9 Hz, 6H).

Synthesis of compound 7b

(E)-1,1'-bis(2-hexyldecyl)-6,6'-bis(4-octylthiophene-2-yl)-[3,3'-biindolinylidene]-2,2'-dione

Compound 20b (1.50 g, 1.73 mmole), compound 16 (1.86 g, 5.18 mmole), tris(dibenzylideneacetone)dipalladium(0) (79.0 mg, 0.08 mmole), and tri(o-tolyl)phosphine (52.5 mg, 0.17 mmole) were added to a 10ml microwave tube. After being capped with Teflon septum, the tube was vacuumed and refilled with nitrogen three times. Anhydrous tetrahydrofurane (3.5ml) was added to the tube via syringe. The parameter of microwave was set to be 90 ^{o}C, 100 W and 15 minutes under

standard mode. After the tube was cooled down, the mixture was concentrated and purified by silica gel column chromatography with solvent mixture hexane: dichloromethane = 2: 1 (v/v) as eluent. Solvents were then removed under reduced pressure, and the residue sticky product was recrystallized in methanol to obtain dark red solid, compound 21b (1.78 g, 94 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, J = 8.4 Hz, 2H), 7.29 – 7.23 (m, 4H), 7.24 (s, 2H), 6.98 – 6.93 (m, 4H), 3.70 (d, J = 7.2 Hz, 4H), 2.63 (t, J = 7.7 Hz, 4H), 1.97 – 1.88 (m, 2H), 1.66 (quintet, J = 7.3 Hz, 4H), 1.44 – 1.18 (m, 68H), 0.91 – 0.82 (m, 18H).

Synthesis of compound 8a

(E)-6,6'-bis(5-bromo-4-octylthiophene-2-yl)-1,1'-bis(2-(2-(2-ethoxyethoxy)ethoxy)ethyl)-[3,3'-biindolinylidene]-2,2'-dione

Compound 21a (3.00 g, 3.09 mmole) was dissolved in tetrahydrofurane (100ml), and the round bottom flask containing reaction mixture was wrapped by a layer of alumina foil to prevent light. 1-bromo-2,5-pyrrolidinedione (1.12 g, 6.33 mmole) was divided into 4 portions and each portion was added to the solution at an interval of 15 minutes. After being stirred in the dark for 12 hours to carry out the reaction, the solution was concentrated and then was purified by a flash column chromatography of silica gel with ether as eluent. Ether was then evaporated under reduced pressure, and the sticky residue was recrystallized in methanol. The dark purple solid, compound 22a (3.0 g, 88%) was obtained after filtration and dried in vacuum oven overnight. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, *J* = 8.4 Hz, 2H), 7.17 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.13 (s, 2H), 7.08 (d, *J* = 1.6 Hz, 2H), 4.03 (t, *J* = 5.6 Hz, 4H), 3.78 (t, *J* = 5.6 Hz, 4H), 3.66 – 3.62 (m, 4H), 3.62 – 3.58 (m, 4H), 3.56 – 3.52 (m, 4H), 3.49 – 3.42 (m, 8H), 2.58 (t, *J* = 7.8 Hz, 3H), 1.64 (quintet, *J* = 7.3Hz, 2H), 1.41 – 1.25 (m, 20H), 1.16 (t, *J* = 7.0 Hz, 6H), 0.89 (t, *J* = 6.9 Hz, 6H).

Synthesis of compound 8b

(E)-6,6'-bis(5-bromo-4-octylthiophene-2-yl)-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione

Compound 21b (3.00 g, 2.38 mmole) was dissolved in tetrahydrofurane (150ml), and the round bottom flask was wrapped by a layer of alumina foil to prevent light. 1-bromo-2,5-pyrrolidinedione (0.87 g, 4.89 mmole) was divided into 4 portions and each portion was added to the solution at an interval of 15 minutes. After being stirred in the dark for 12 hours to carry out the reaction, the solution was concentrated and then it was purified by a flash column chromatography of silica gel with solvent mixture hexane: dichloromethane = 2: 1 (v/v) as eluent. Solvents were then

evaporated under reduced pressure, and the sticky residue was recrystallized in methanol. The dark purple solid, compound 22b (3.0 g, 88%) was obtained after filtration and dried in vacuum oven overnight. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, *J* = 8.4 Hz, 2H), 7.18 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.08 (s, 2H), 6.85 (d, *J* = 1.6 Hz, 2H), 3.68 (d, *J* = 7.3 Hz, 4H), 2.58 (t, *J* = 7.6 Hz, 4H), 1.95 – 1.85 (m, 2H), 1.63 (quintet, *J* = 7.4 Hz, 4H), 1.45 – 1.16 (m, 68H), 0.91 – 0.84 (m, 18H).

Synthesis of compound 9

2,5-bis(trimethylstannyl)thiophene

To the solution of thiophene (4.21 g, 0.05 mole) dissolved in anhydrous tetrahydrofurane (100ml), n-butyllithium (40 ml, 0.10 mole) was added dropwise via syringe. The mixture was reacted at -40℃ in dry ice/acetonitrile bath. Trimethyltin chloride (100 ml, 0.10 mol) was add to the solution, and the coolant was removed when the transfer finished. The solution was reacted at ambient temperature under stirring for 12 hours. The solution was concentrated and then extracted with hexane and distilled water several times. The combined organic layers were dried over anhydrous magnesium sulfate. After filtration, the solution was concentrated by rotary evaporator. The crude oil was recrystallized from cold methanol to obtain white solid, compound 23 (17.62 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 2H), 0.37 (s, 18H).

Synthesis of compound 10

5,5'-bis(trimethylstannyl)-2,2'-bithiophene

To a solution of 2,2'-bithiophene (8.31 g, 0.05 mole) in anhydrous tetrahydrofurane, n-butyllithium (40 ml, 0.10 mole) was added dropwise via syringe and the solution was cooled down by dry ice / acetonitrile bath. After the solution was reacted at -40℃ under stirring for 2 hours, trimethyltin chloride (100 ml, 0.10 mol) was added to the solution. Coolant was removed when the transfer finished, and the mixture was reacted at ambient temperature under stirring overnight. The solution was concentrated and extracted with hexane and distilled water several times. The combined organic layers were dried over anhydrous magnesium sulfate. Hexane was evaporated under reduced pressure. The yellow residue was recrystallized in methanol to obtain white solid, compound 24 (22.87 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 3.3 Hz, 2H), 7.09 (d, *J* = 3.3 Hz, 2H), 0.39 (s, 18H).

Synthesis of compound 11

3-(bromomethyl)thiophene

A 250 ml round bottom flask was evacuated by vacuum system and refilled the

nitrogen to remove the moisture in the flask. Next, thiophene-3-ylmethanol (5 g, 43.8 mmole) and 100 ml dry dichloromethane were placed into the flask. The flask was placed in an ice bath. Then phosphorus tribromide (4.14 ml, 44.0 mmole) was added into the flask over a 15 min period. The mixture was stirred under room temperature for 5 hours, then quenched with sodium bicarbonate solution. Then the mixture was extracted by hexane and distilled water. The organic layer was collected, dried by anhydrous magnesium sulfate, and filtered by filter paper. The filtrate was collected and the hexane was removed by rotary evaporator. After that, the condensed mixture passed through a plug of celite using dichloromethane as eluent. Finally, the mixture was purified by a plug of silica gel using hexane as eluent to obtain pale yellow oil, compound 25 (5.2 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 2H), 7.13 (dd, J = 4.9, 1.4 Hz, 1H), 4.53 (s, 2H).

Synthesis of compound 12

1-(thiophene-3-yl)-2,5,8,11-tetraoxatridecane

A 250 ml round bottom flask was evacuated by vacuum system and refilled the nitrogen to remove the moisture in the flask. Next, 2-(2-(2-ethoxyethoxy)ethoxy)ethanol (5.00 g, 28.10 mmole) and 125 ml anhydrous tetrahydrofurane were placed in the flask. Then sodium hydride (0.80 g, 33 mmole) was added into the flask. After hydrogen gas evolution had ceased, compound 25 (4.80 g, 27.10 mmole) was added into the flask. The mixture was stirred under room temperature for 5 hours. The mixture was extracted by ethyl acetate and distilled water. The organic layer was collected, the ethyl acetate was removed by rotary evaporator. The condensed mixture was purified through column chromatography (ethyl acetate as eluent, silica gel) to obtain pale yellow oil, compound 26 (4.10 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, J = 4.9, 3.0 Hz, 1H), 7.21 (m, 1H), 4.57 (s, 2H), 3.56-3.70 (m, 12H), 3.50(q, J = 7.0 Hz, 2H), 1.2 (t, J = 7.0 Hz, 3H).

Synthesis of compound 13

1-(2-bromothiophene-3-yl)-2,5,8,11-tetraoxatridecane

Compound 26 (3.00 g, 10.93 mmole) and 100 ml tetrahydrofuran was placed in a 250 ml round bottom flask, and the flask was put into ice bath. Next, 1-bromo-2,5-pyrrolidinedione (1.95 g, 10.93 mmole) was added into the flask. The mixture was stirred under 0 ^{o}C for 2 hours. After the reaction, the tetrahydrofuran was removed by rotary evaporator. The condensed mixture was purified through column chromatography (ethyl acetate as eluent, silica gel) to obtain yellow oil, compound 27 (3.28 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 5.6 Hz, 1H), 7.00 (d, J = 5.6

Hz, 1H), 4.50 (s, 2H), 3.56-3.70 (m, 12H), 3.52(q, *J* = 7.0 Hz, 2H), 1.2 (t, *J* = 7.0 Hz, 3H).

Synthesis of compound 14

3,3''-di(2,5,8,11-tetraoxatridecyl)-2,2':5',2''-terthiophene

Compound 27 (1.00 g, 2.83 mmole), compound 23 (0.58 g, 1.42 mmole), tris(dibenzylideneacetone)dipalladium(0) (64.89 mg, 0.07 mmole), and tri(o-tolyl)phosphine (43.26 mg , 0.14 mmole), and 4 ml degassed tetrahydrofuran were placed in a 10ml microwave vessel then the vessel was put in the microwave reactor, and parameters for the reaction were set at 100 ^{o}C, 100 W, and 45 min. The mixture was purified through column chromatography (ethyl acetate as eluent, silica gel) to obtain yellow oil, compound 28 (714 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 5.2 Hz, 2H), 7.16 (s, 2H), 7.14 (d, *J* = 5.1 Hz, 2H), 4.63 (s, 4H), 3.56-3.70 (m, 24H), 3.51(q, *J* = 7.0 Hz, 4H), 1.19 (t, *J* = 7.0 Hz, 6H).

Synthesis of compound 15

3,3'''-di(2,5,8,11-tetraoxatridecyl)-2,2':5',2'':5'',2'''-quaterthiophene

Compound 27 (1.00 g, 2.83 mmole), compound 24 (0.70 g, 1.42 mmole), tris(dibenzylideneacetone)dipalladium(0) (64.89 mg, 0.07 mmole), and tri(o-tolyl)phosphine (43.26 mg , 0.14 mmole), and 4 ml degassed tetrahydrofuran were placed in a 10ml microwave vessel then the vessel was put in the microwave reactor, and parameters for the reaction were set at 100 ^{o}C, 100 W, and 45 min. The mixture was purified through column chromatography (ethyl acetate as eluent, silica gel) to obtain orange oil, compound 29 (828 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 5.2 Hz, 2H), 7.14 (m, 6H), 4.64 (s, 4H), 3.56-3.70 (m, 24H), 3.51 (q, *J* = 7.0 Hz, 4H), 1.20 (t, *J* = 7.0 Hz, 6H).

Synthesis of compound 16

(3,3''-di(2,5,8,11-tetraoxatridecyl)-[2,2':5',2''-terthiophene]-5,5''-diyl)bis(trimethylstannane)

A 150 ml round bottom flask was evacuated by vacuum system and refilled the nitrogen to remove the moisture in the flask. Next, compound 28 (500 mg, 0.80 mmole) and 50 ml anhydrous tetrahydrofuran were placed in the flask. After that, the flask was put in -78^{o}C dry ice bath. Then, 0.64 ml 2.5M n-butyllithium in hexane solution (1.60 mmole) was added into the flask and the solution was stirred for 2 hours. The -78^{o}C dry ice bath was removed and the solution was stirred at room temperature for 1 hour. Then the flask was put in -78^{o}C dry ice bath again and 1.60 ml 1M trimethyltin chloride in tetrahydrofuran solution (1.60 mmole) was added into the

flask. After complete adding the trimethyltin chloride solution, the -78^{o}C dry ice bath was removed and the solution was stirred at room temperature for 12 hours. The mixture was extracted by ethyl acetate and distilled water. The organic layer was collected, dried over anhydrous magnesium sulfate, and filtered by filter paper. The filtrate was collected and the ethyl acetate was removed by rotary evaporator. Finally, the condensed mixture can be further purified by column chromatography (ethyl acetate as eluent, celite gel) to obtain yellow oil, compound 30 (611 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 2H), 7.14 (s, 2H), 4.64 (s, 4H), 3.56-3.70 (m, 24H), 3.51 (q, *J* = 7.0 Hz, 4H), 1.20 (t, *J* = 7.0 Hz, 6H), 0.38 (s, 18H).

Synthesis of compound 17
(3,3'''-di(2,5,8,11-tetraoxatridecyl)-[2,2':5',2'':5'',2'''-quaterthiophene]-5,5'''-diyl)bis(trimethylstannane)

Compound 29 (500 mg, 0.70 mmole), 0.56 ml 2.5M n-butyllithium in hexane solution (1.40 mmole), and 1.40 ml 1M trimethyltin chloride in tetrahydrofuran solution (1.40 mmole) were used to do the reaction. Following the synthetic procedure of compound 30, one obtained orange oil, compound 31 (508 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 2H), 7.12 (dd, *J* = 8.8, 3.8 Hz, 4H), 4.64 (s, 4H), 3.56-3.70 (m, 24H), 3.51 (q, *J* = 7.0 Hz, 4H), 1.20 (t, *J* = 7.0 Hz, 6H), 0.38 (s, 18H).

General procedure for polymerization of oligothiophene-isoindigo based CPs.

The two monomers (0.2 mmole each), tris(dibenzylideneacetone)dipalladium(0) (10 mg, 0.01 mmole), tris(*o*-tolyl)phosphine (15 mg, 0.05 mmole) and 4 ml degassed tetrahydrofuran were placed in a 10ml microwave vessel to do the Still coupling polymerization by microwave reactor. The parameters for the reaction were set at 100 ^{o}C, 100 W, and 15 min. After polymerization, the polymers were precipitated in methanol then subjected to purification via Soxhlet extractions using a specific solvent sequence. For P3T(R_8)I($R_{b\text{-}16}$) and P3T(R_8)I(E), the solvent sequence is methanol→hexane→chloroform. For P4T(R_8)I($R_{b\text{-}16}$) and P4T(R_8)I(E), the solvent sequence is methanol→hexane→tetrahydrofurane→chloroform. For P3T(E)I(E), the solvent sequence is hexane→methanol→chloroform. For P4T(E)I(E), the solvent sequence is hexane→methanol→ethyl acetate→chloroform. Then we collected the chloroform solutions, removed the chloroform by rotary evaporator, and finally acquired pure polymers. The information of the monomers used in polymerization and the yield is shown in **Table S1.**

Table S1. Monomers used in polymerization and polymer yield

Polymers	Monomer 1 (Compound)	Monomer 2 (Compound)	Yield
P3T(R_8)I($R_{b\text{-}16}$)	8b	9	85%
P3T(R_8)I(E)	8a	9	82%
P3T(E)I(E)	16	6a	54%
P4T(R_8)I($R_{b\text{-}16}$)	8b	10	65%
P4T(R_8)I(E)	8a	10	62%
P4T(E)I(E)	17	6a	50%

2. Experiment Method

Gel permeation chromatography (GPC). The molecular weights of the series of P3TI and P4TI polymers were measured by Waters GPC (Viscotek GPCMax) using chloroform as an eluent at 40 °C. The instrument was equipped with two Waters Styragel columns (HR3 and HR4E), a refractive index detector (Waters 2414), and a dual-wavelength absorbance detector (Waters 2487). The wavelengths were set at 254 and 465 nm.

Molecular orbital simulation. Molecular simulation was performed on Gaussian 09W package. B3LYP/6-31G** method was employed for all the calculation. Due to limited computational resource, only single repeat unit of P3TI and P4TI polymers was calculated.

UV-Vis absorption spectra (UV-Vis). The UV-Vis spectra of the series of P3TI and P4TI polymer films were measured by Perkin Elmer UV-Vis instrument (Lambda 35). Scan range: 1000 ~ 300 nm. Polymer films for UV-Vis analysis: Drawing 70 μl from 1 ml polymer solutions (solvent: chloroform, concentration: 10 mg/ml) and dropping

on the glass substrates (size: 1.25 cm*1.25 cm). After that, the glass substrates were spun (spin rate: 1000 rpm) by spin coater (Laurell Tec., WS-400A) to obtain the polymer films (thickness: ~100 nm) and the films were annealed at 200 ^{o}C for 1 h.

Thermalgravimetric analysis (TGA). TGA experiment was performed by TA instrument (Q50). Polymer weight loss was measured by heating the polymer at a rate of 10 ^{o}C/min from 25 ^{o}C to 600 ^{o}C.

Differential scanning calorimetry (DSC). DSC experiment was performed by TA instrument (Q200). The procedure was set to be as following: (1) equilibrate at 200 ^{o}C (2) isothermal for 1 hour (3) equilibrate at 0 ^{o}C (4) isothermal for 5 min (5) heat from 0 ^{o}C ~ 320 ^{o}C with heating rate of 10 ^{o}C/min for P3T(R_8)I($R_{b\text{-}16}$), P3T(R_8)I(E), P4T(R_8)I($R_{b\text{-}16}$), and P4T(R_8)I(E); heat from 0 ^{o}C~ 220 ^{o}C with heating rate of 10 ^{o}C/min for P3T(E)I(E), and P4T(E)I(E). Only heating round (step 5) profiles were used to analyze the thermal properties of the polymers.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) The GIWAXS profile of the series of P3TI and P4TI polymers were measured by the GIWAXS instrument provided from Beamline 13A and 17A in National Synchrotron Radiation Research Center (NSRRC). The incident angle was 0.2^{o}. The annealed polymer films for GIWAXS analysis were prepared as follows: 60 μl from 1 ml polymer solutions (solvent: chloroform, concentration: 10 mg/ml) was drop-casted on the silicon wafers (size: 1 cm*1 cm, Summit Tech corp., 100 ± 0.5°, P/boron). Then, the polymer films were annealed at 200 ^{o}C for 1 h.

3. Molecular Orbital Simulation Results

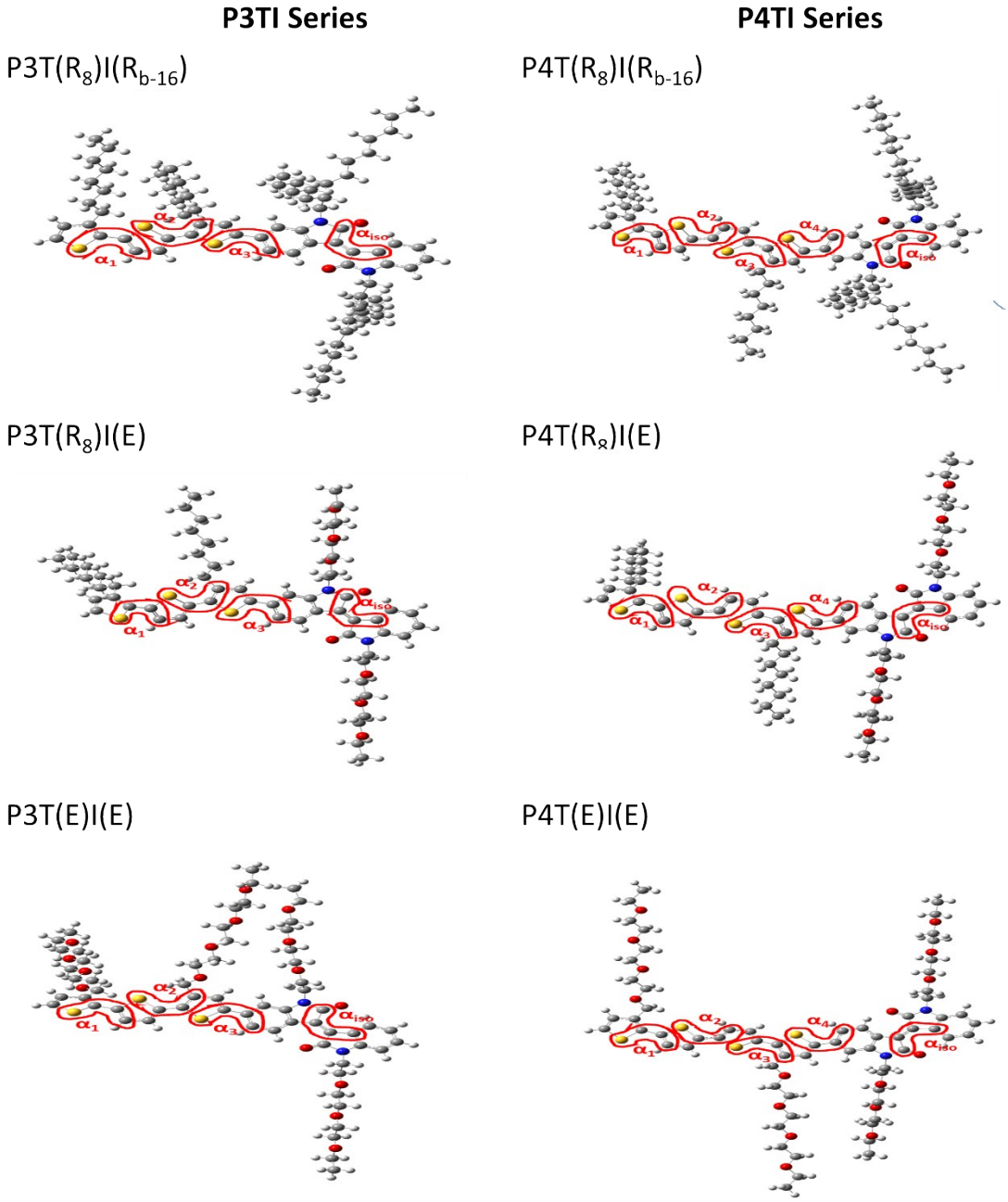


Figure S1. Molecular simulation results, including front view of molecular plan, of PnTI polymers.

Table S2. Summary of molecular simulation of PnTI polymers

Polymer	α_1 (°)	α_2 (°)	α_3 (°)	α_4 (°)	α_{iso} (°)	α_{total}(°)	curvature
P3T(R_8)I($R_{b\text{-}16}$)	-33	-34	24	-	-12	-55	S-shaped
P3T(R_8)I(E)	47	-25	21	-	-12	31	S-shaped
P3T(E)I(E)	32	31	-20	-	-12	31	S-shaped
P4T(R_8)I($R_{b\text{-}16}$)	44	-17	16	-21	-12	10	linear
P4T(R_8)I(E)	45	-15	26	-21	-12	23	linear
P4T(E)I(E)	-33	-11	25	17	-12	9	linear

4. [1]H NMR data for all synthetic intermediates and monomers

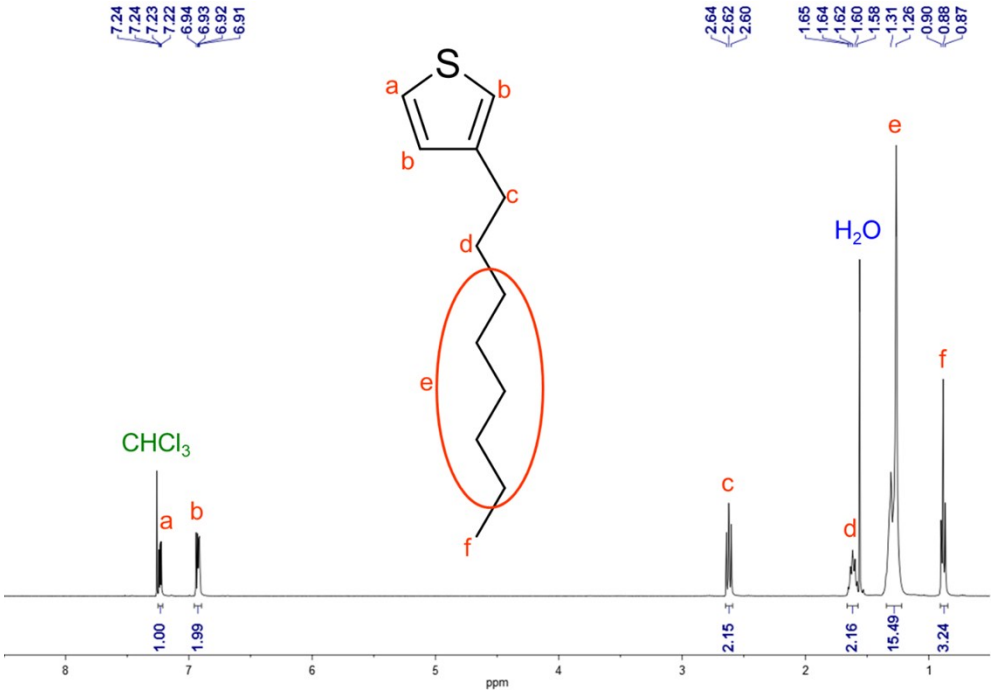


Figure S2. [1]H NMR of compound 1

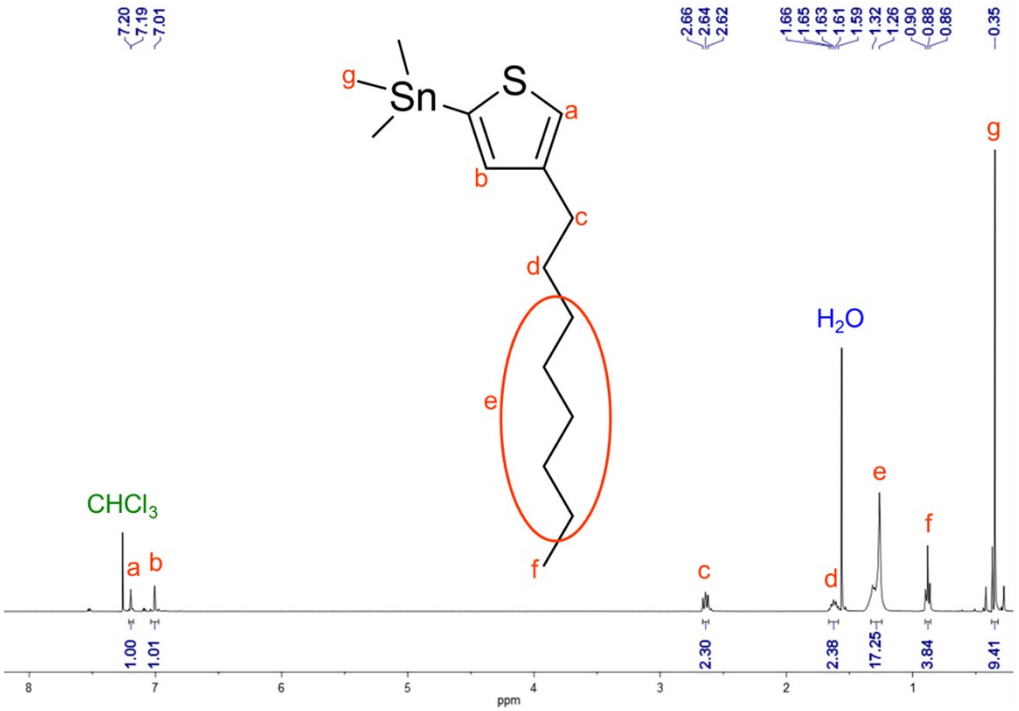


Figure S3. [1]H NMR of compound 2

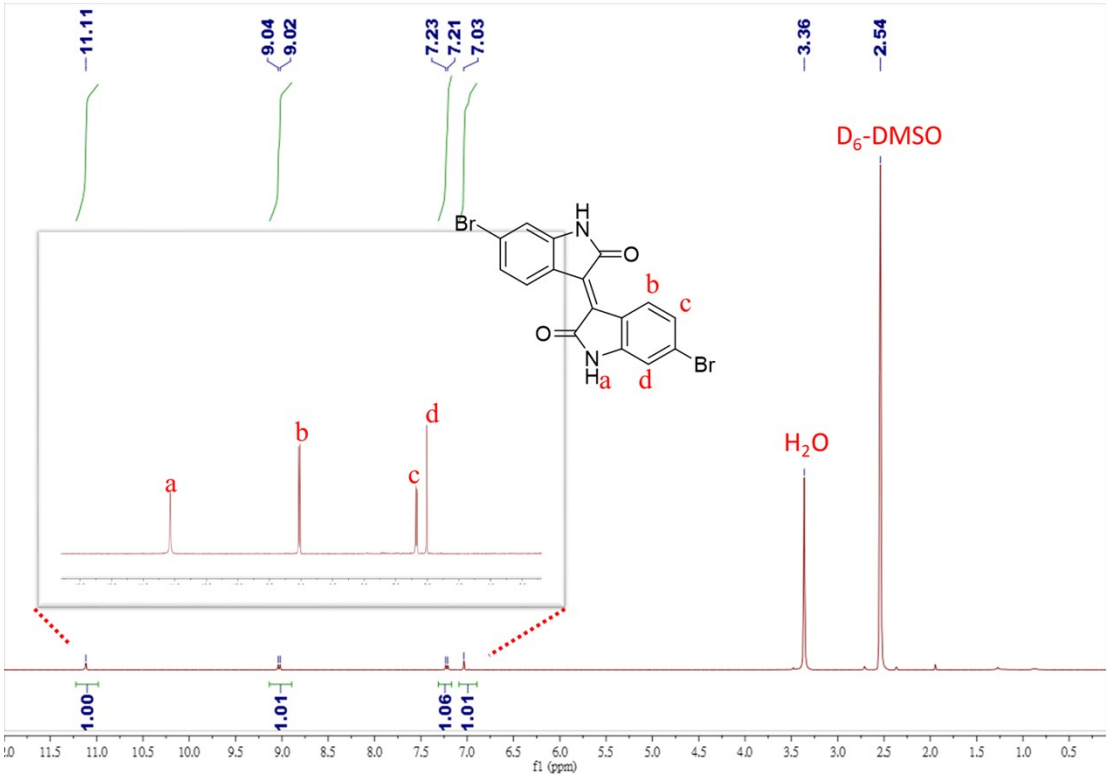


Figure S4. [1]H NMR of compound 3

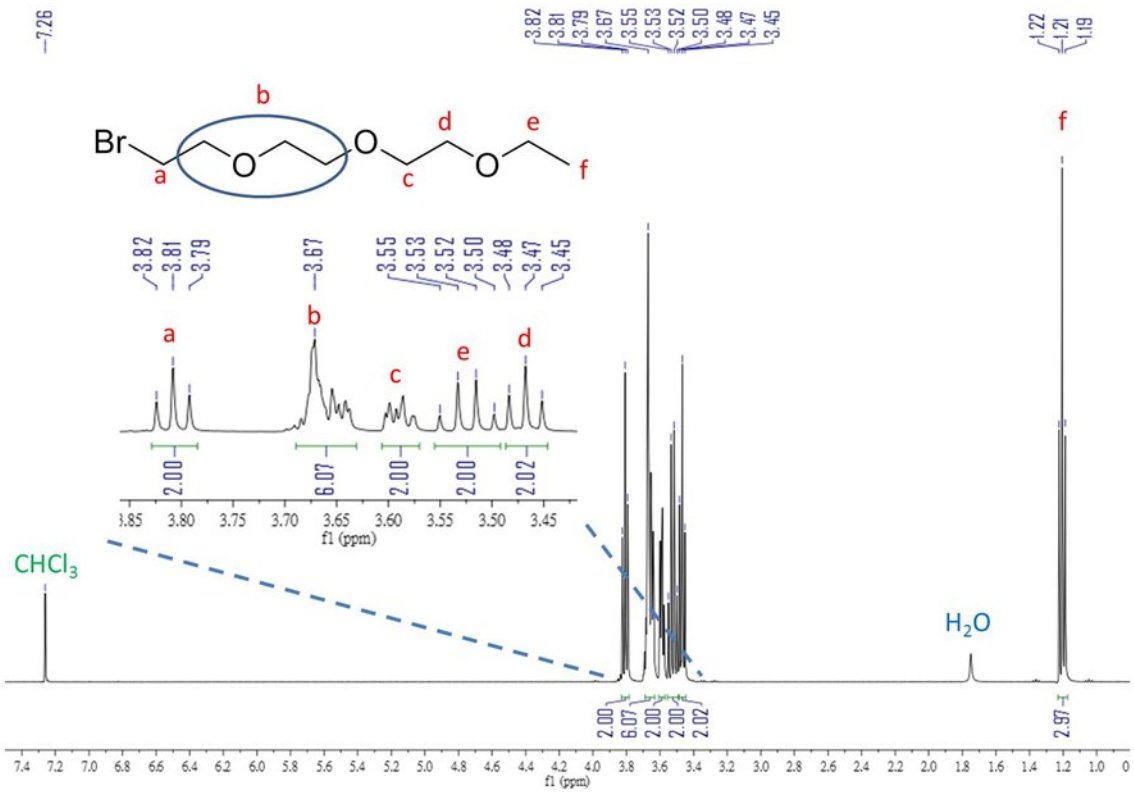


Figure S5. [1]H NMR of compound 4

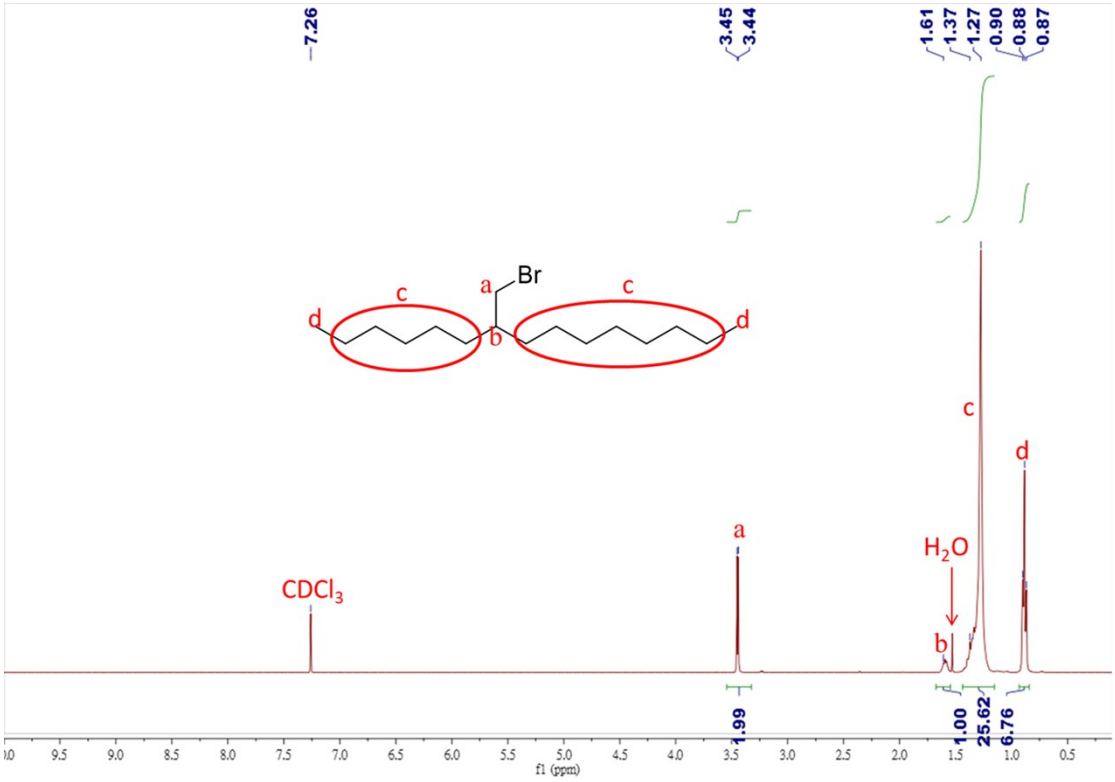


Figure S6. [1]H NMR of compound 5

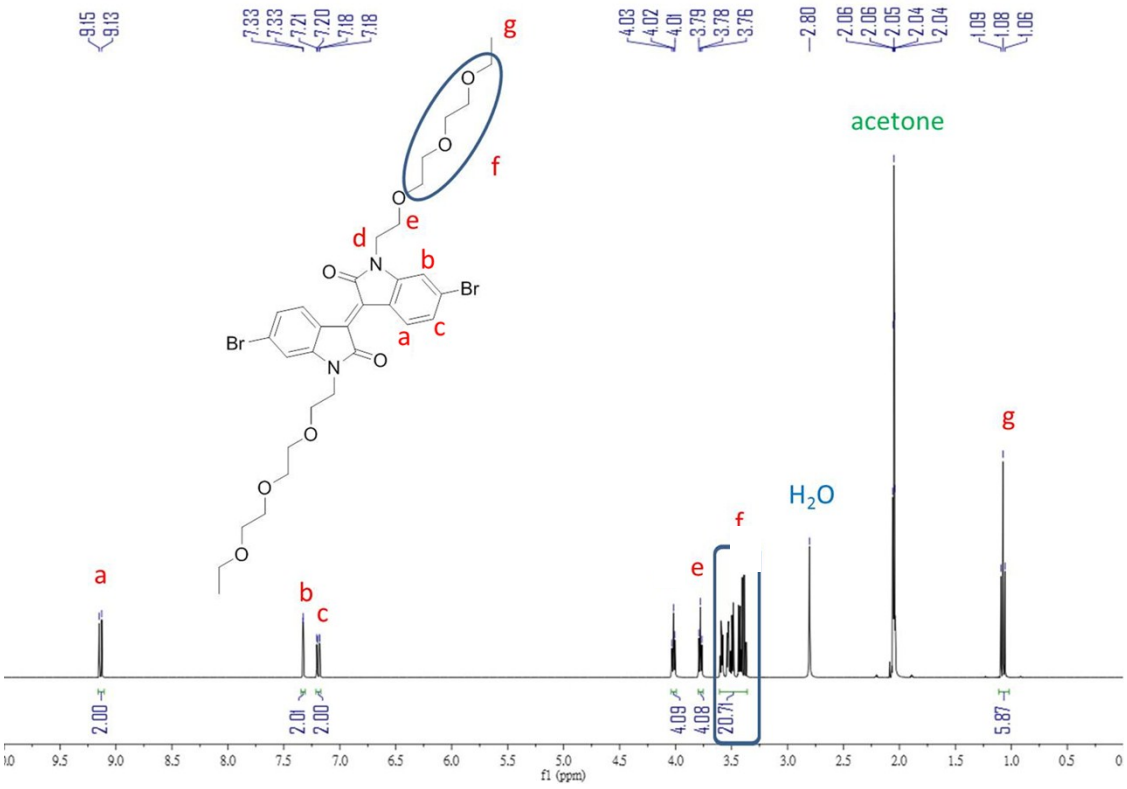


Figure S7. [1]H NMR of compound 6a

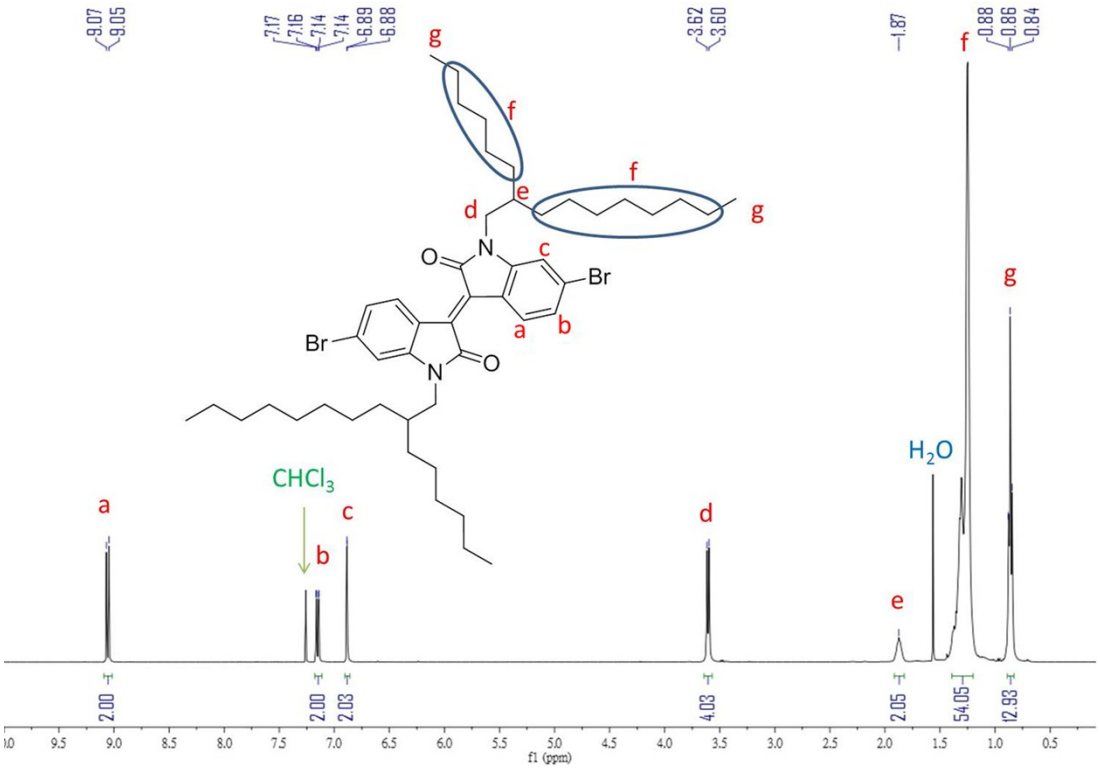


Figure S8. [1]H NMR of compound 6b

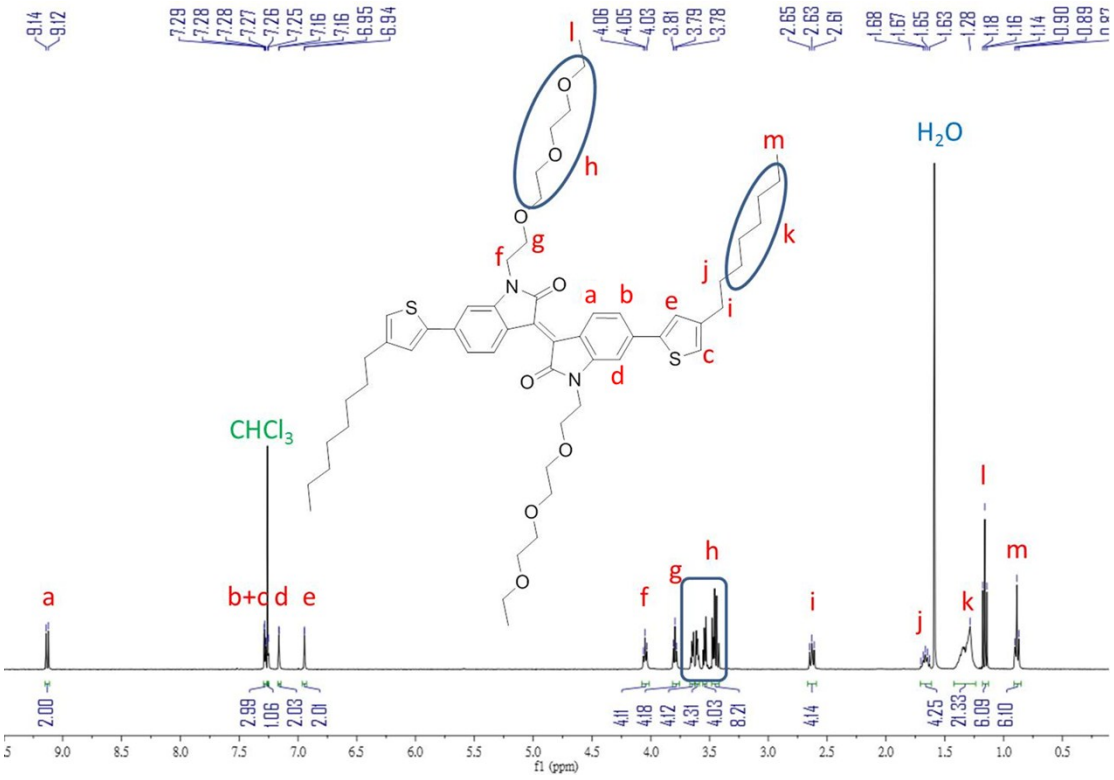


Figure S9. [1]H NMR of compound 7a

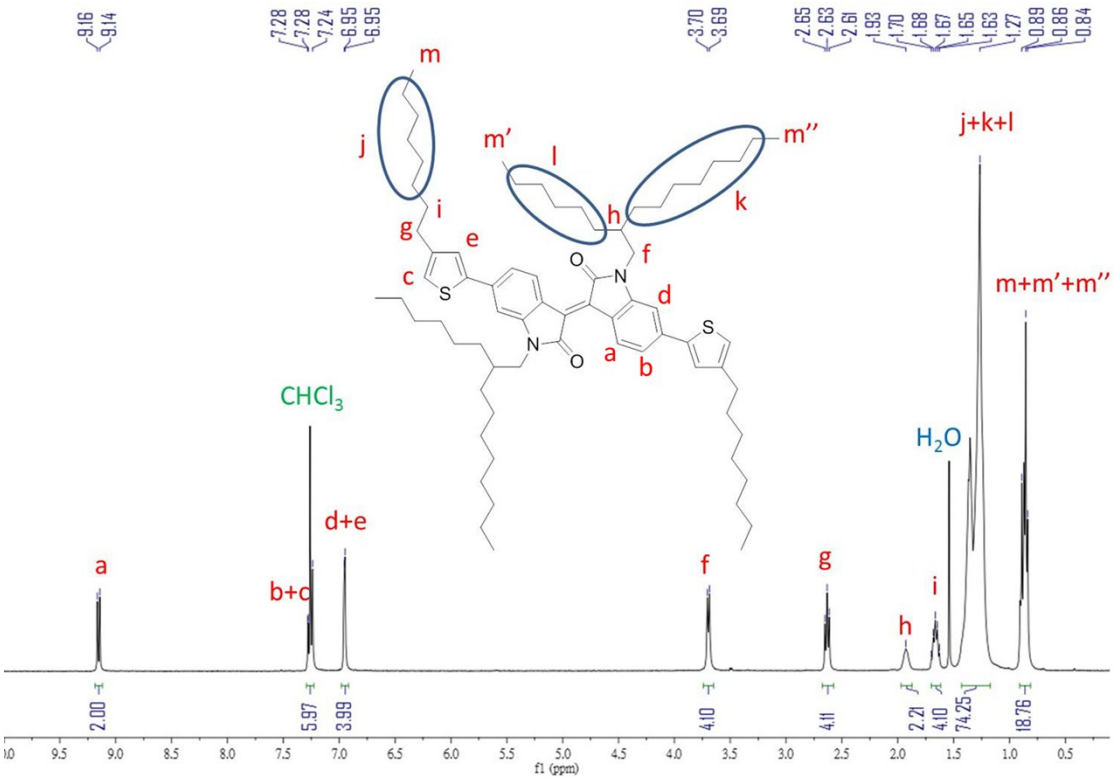


Figure S10. [1]H NMR of compound 7b

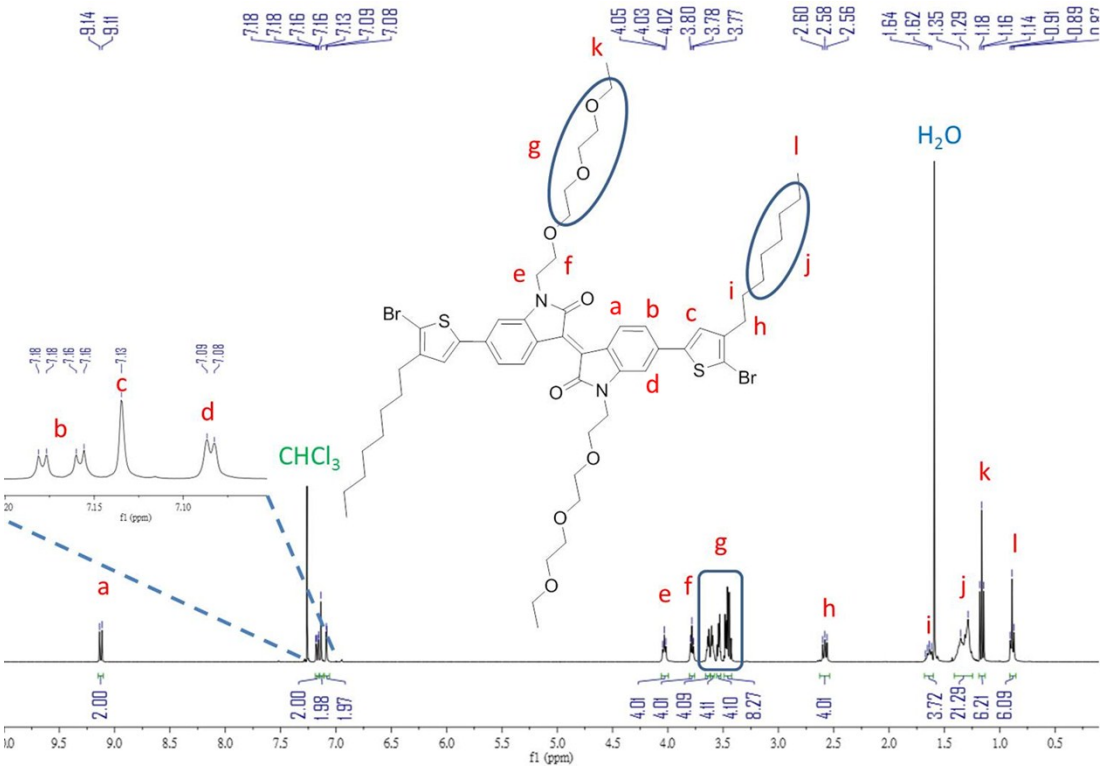


Figure S11. [1]H NMR of compound 8a

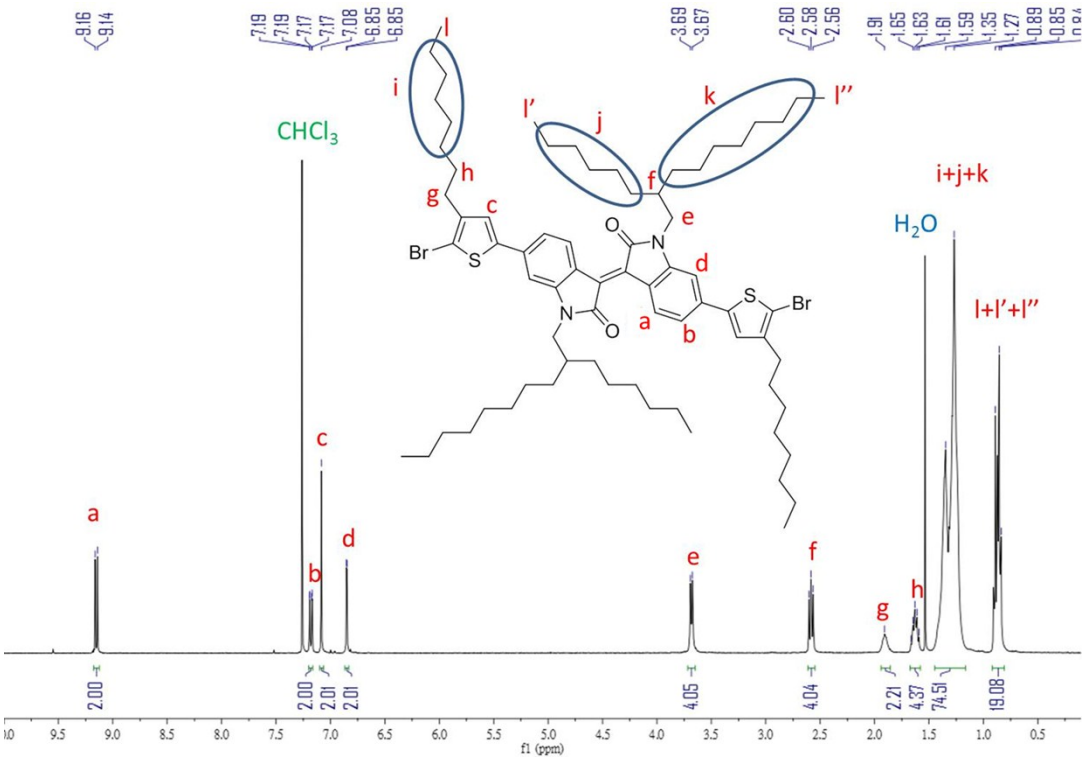


Figure S12. ^{1}H NMR of compound 8b

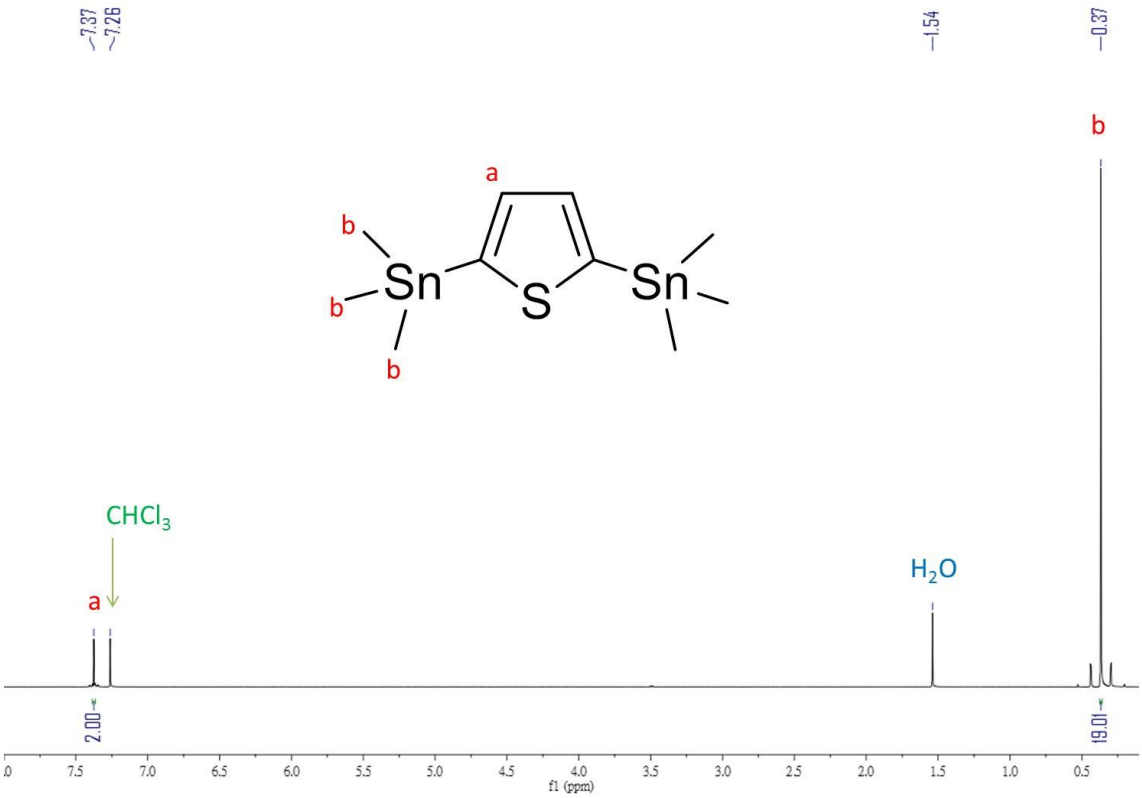


Figure S13. ^{1}H NMR of compound 9

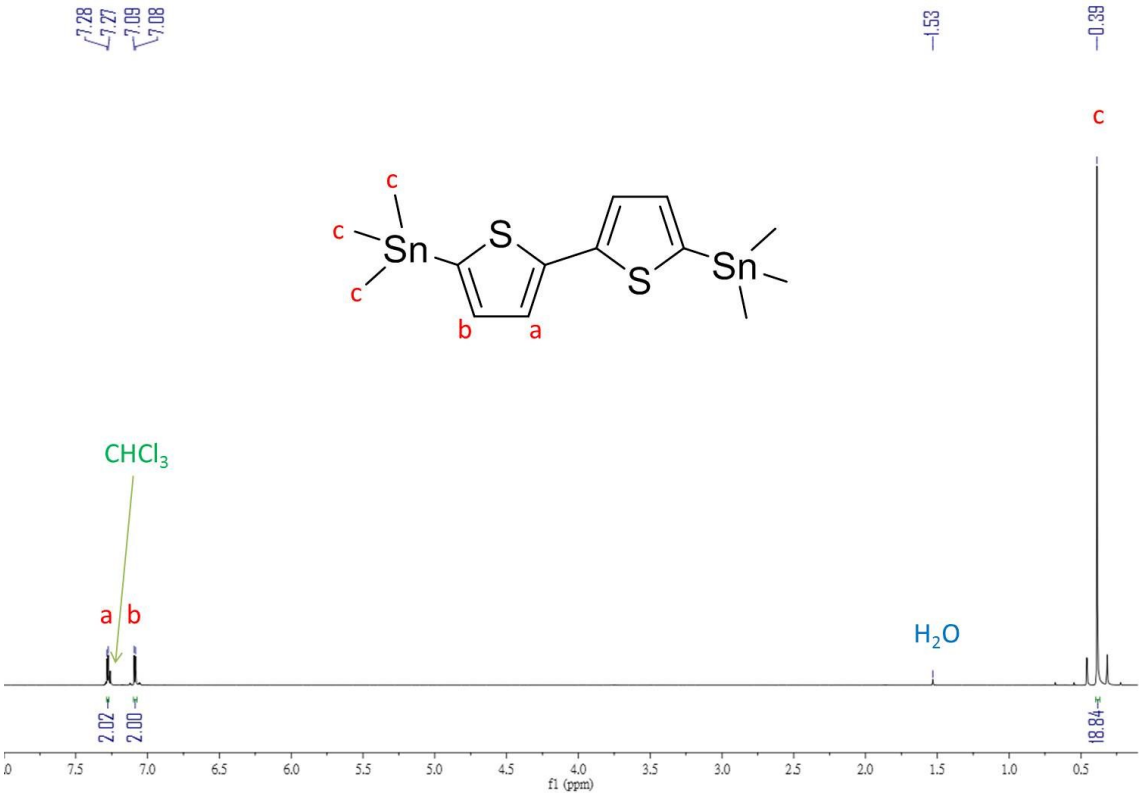


Figure S14. [1]H NMR of compound 10

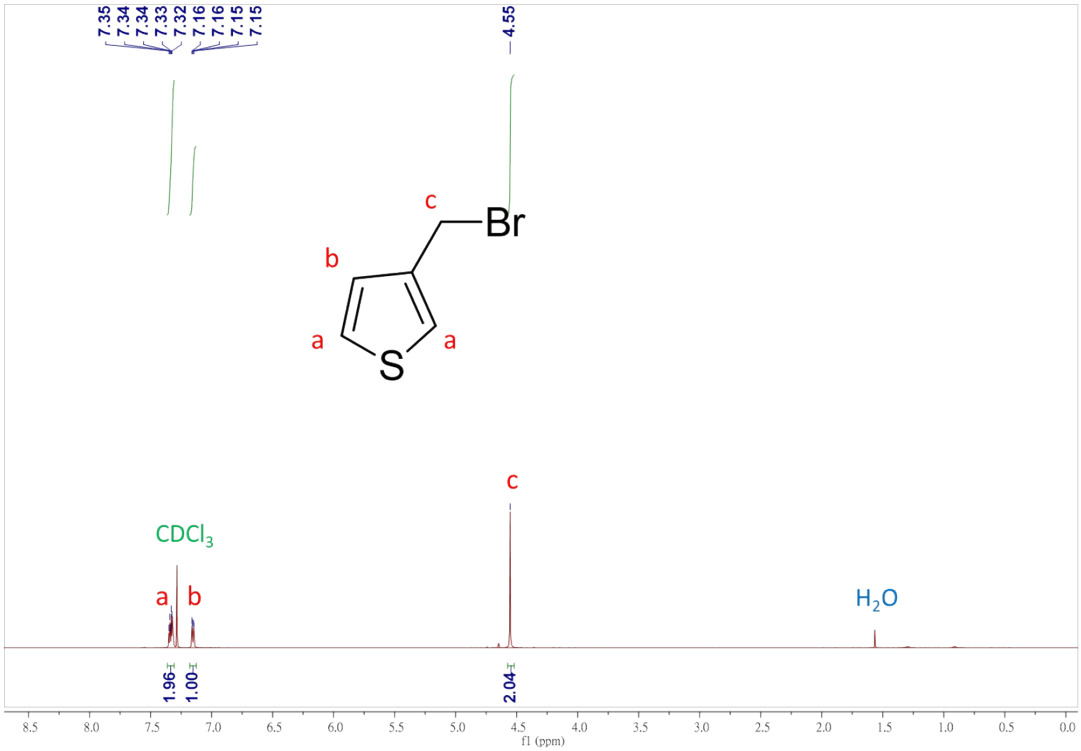


Figure S15. [1]H NMR of compound 11

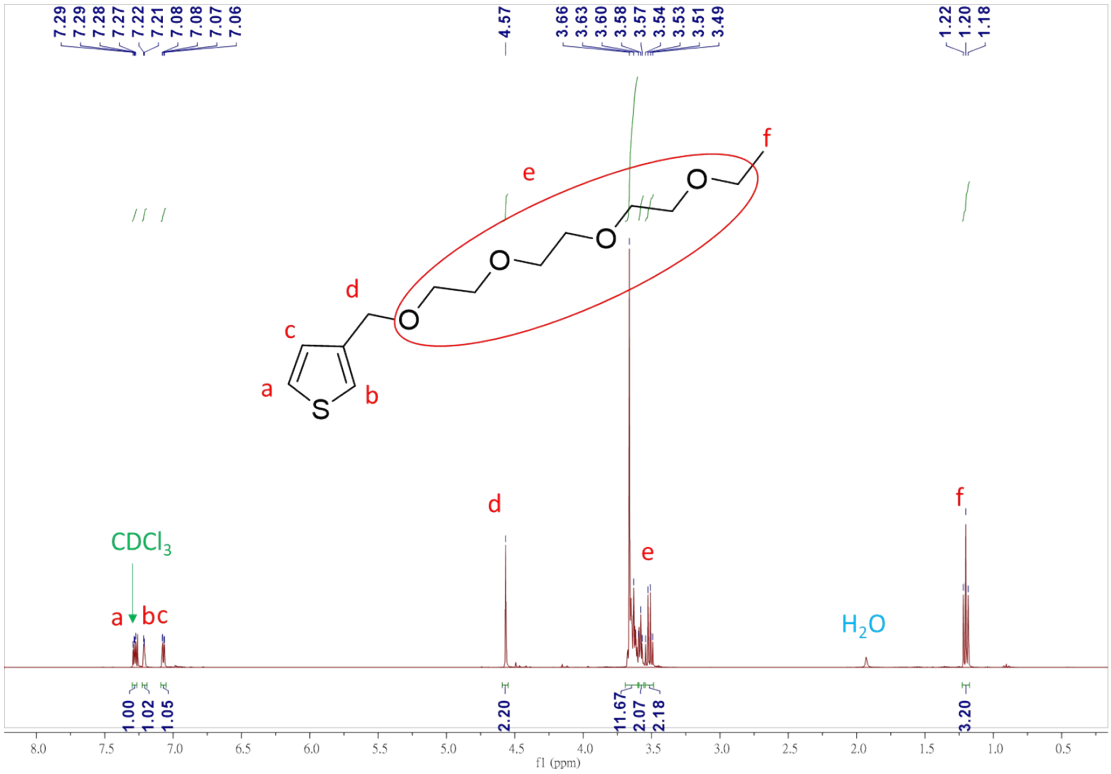


Figure S16. ^{1}H NMR of compound 12

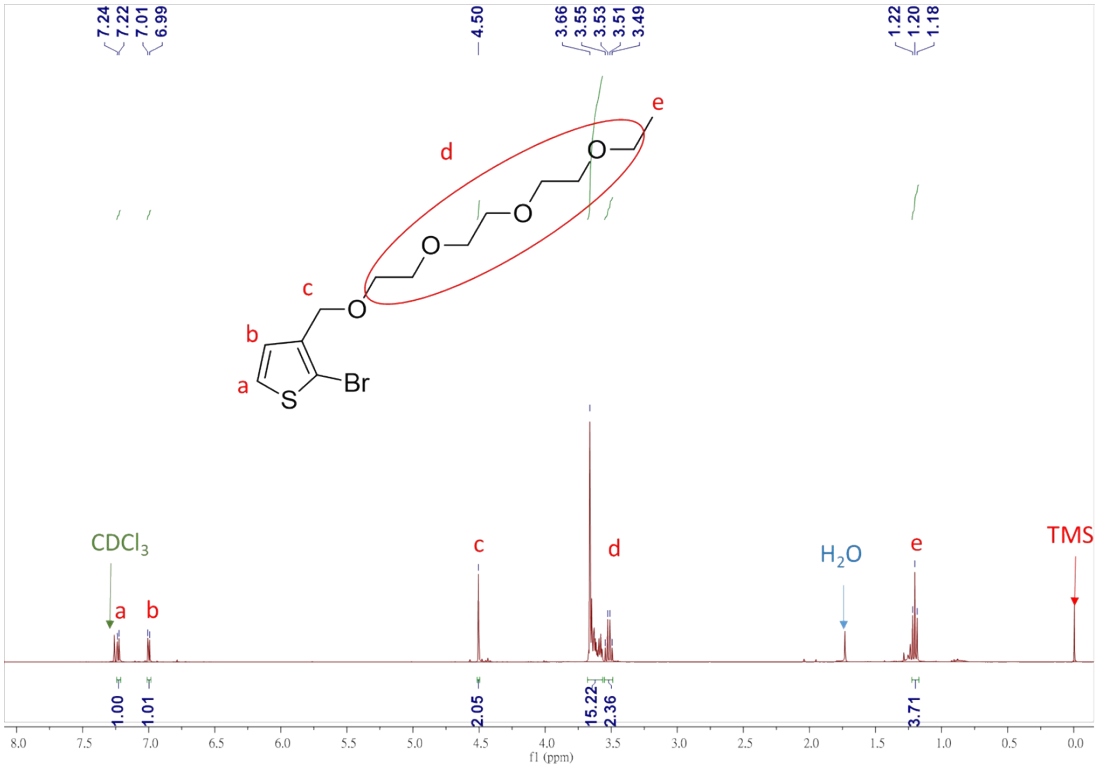


Figure S17. ^{1}H NMR of compound 13

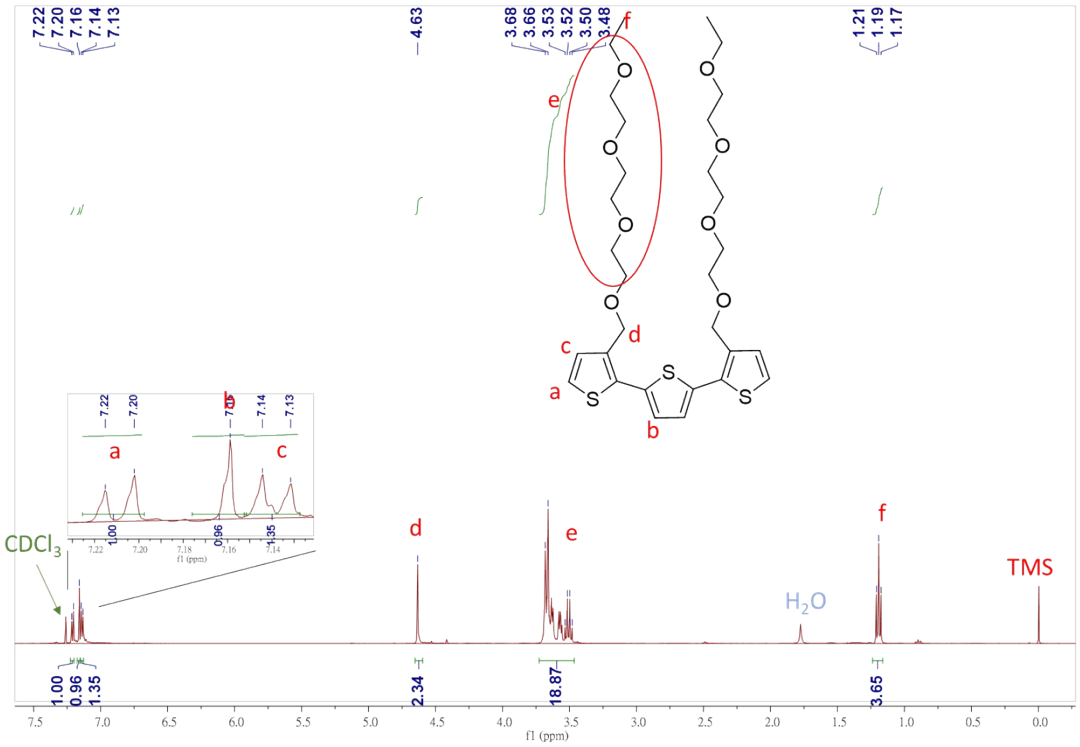


Figure S18. ^{1}H NMR of compound 14

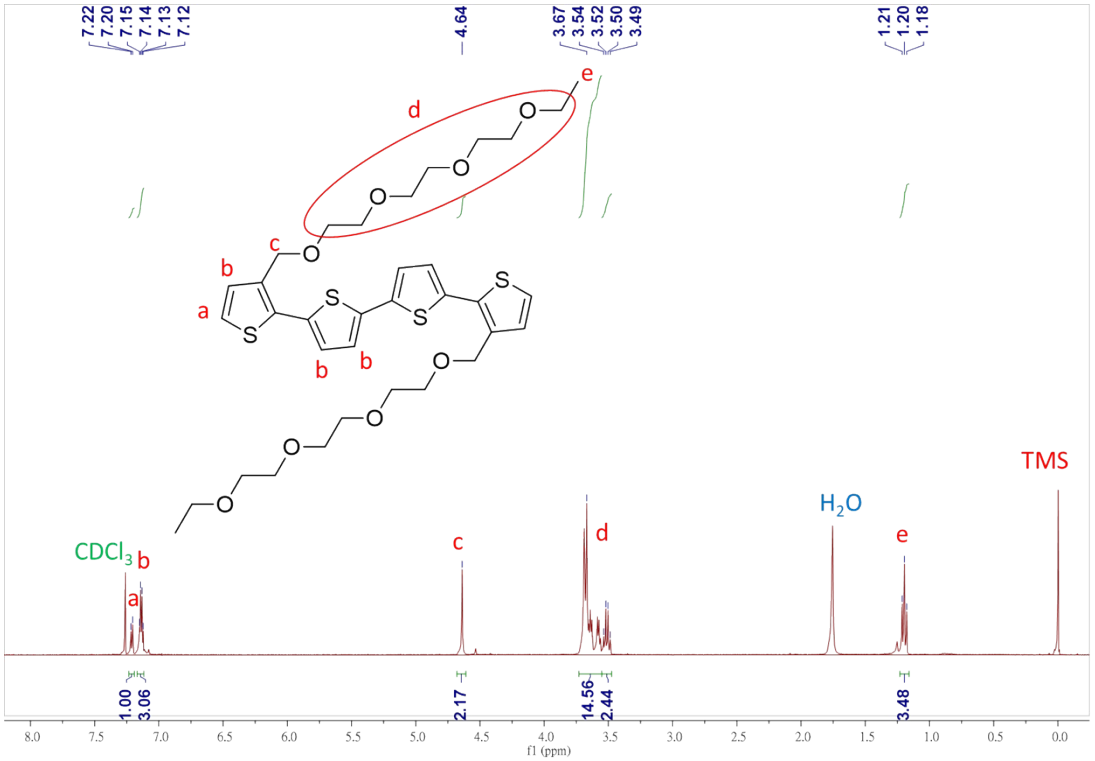


Figure S19. ^{1}H NMR of compound 15

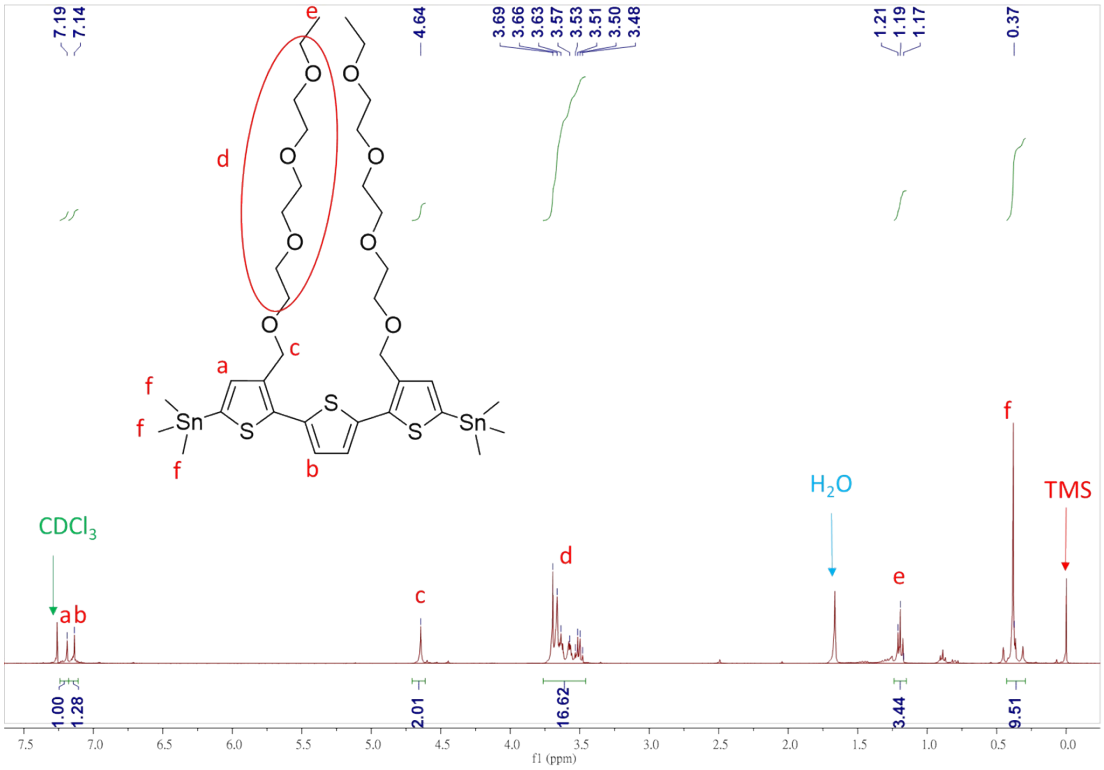


Figure S20. ^{1}H NMR of compound 16

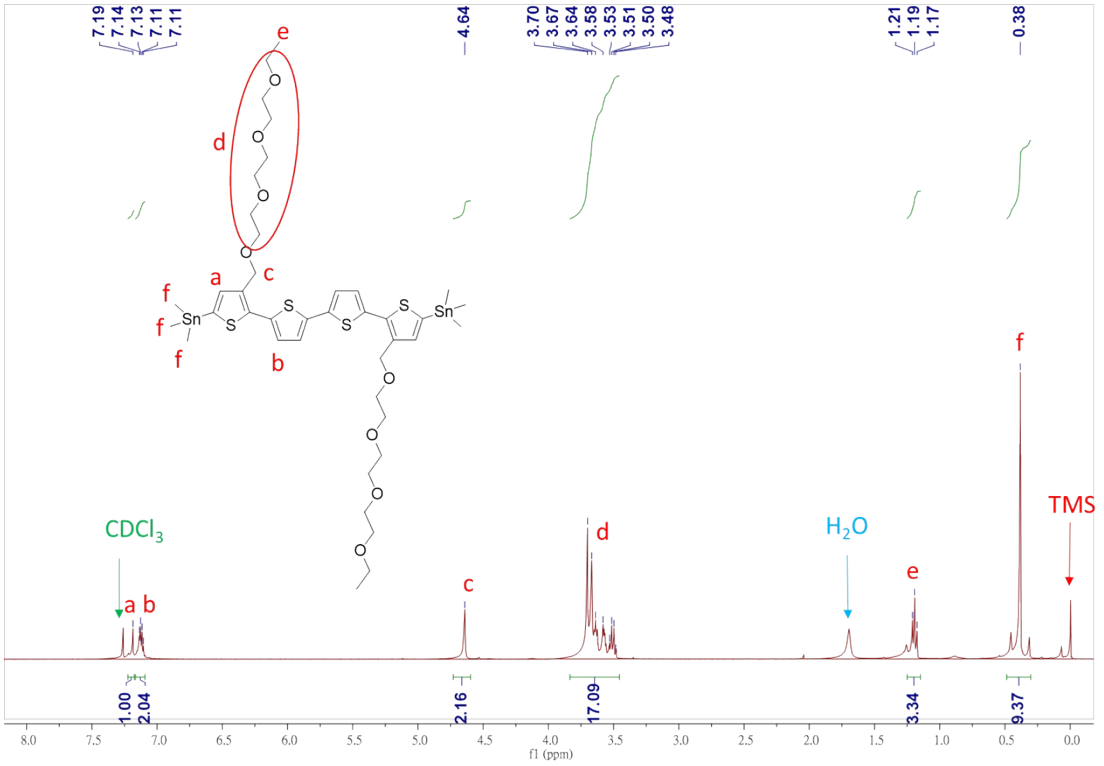


Figure S21. ^{1}H NMR of compound 17