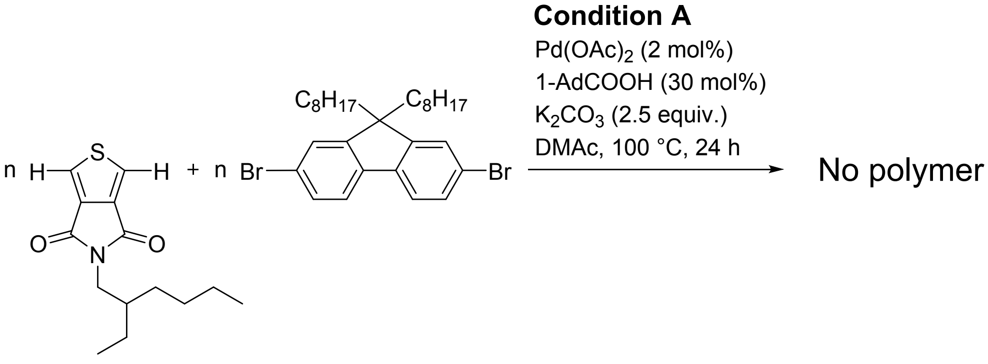
Supporting Information for

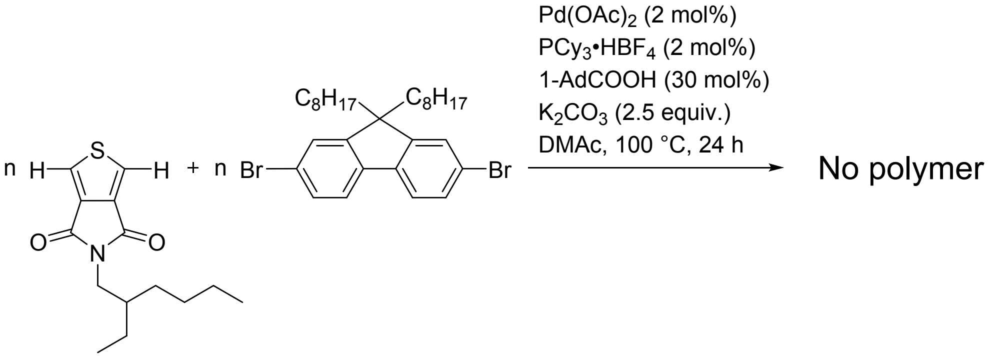
The effect of solvent in direct arylation polycondensation of substituted thiophenes

Junpei Kuwabara, Kohtaro Yamazaki, Takuya Yamagata, Wataru Tsuchida, Takaki Kanbara

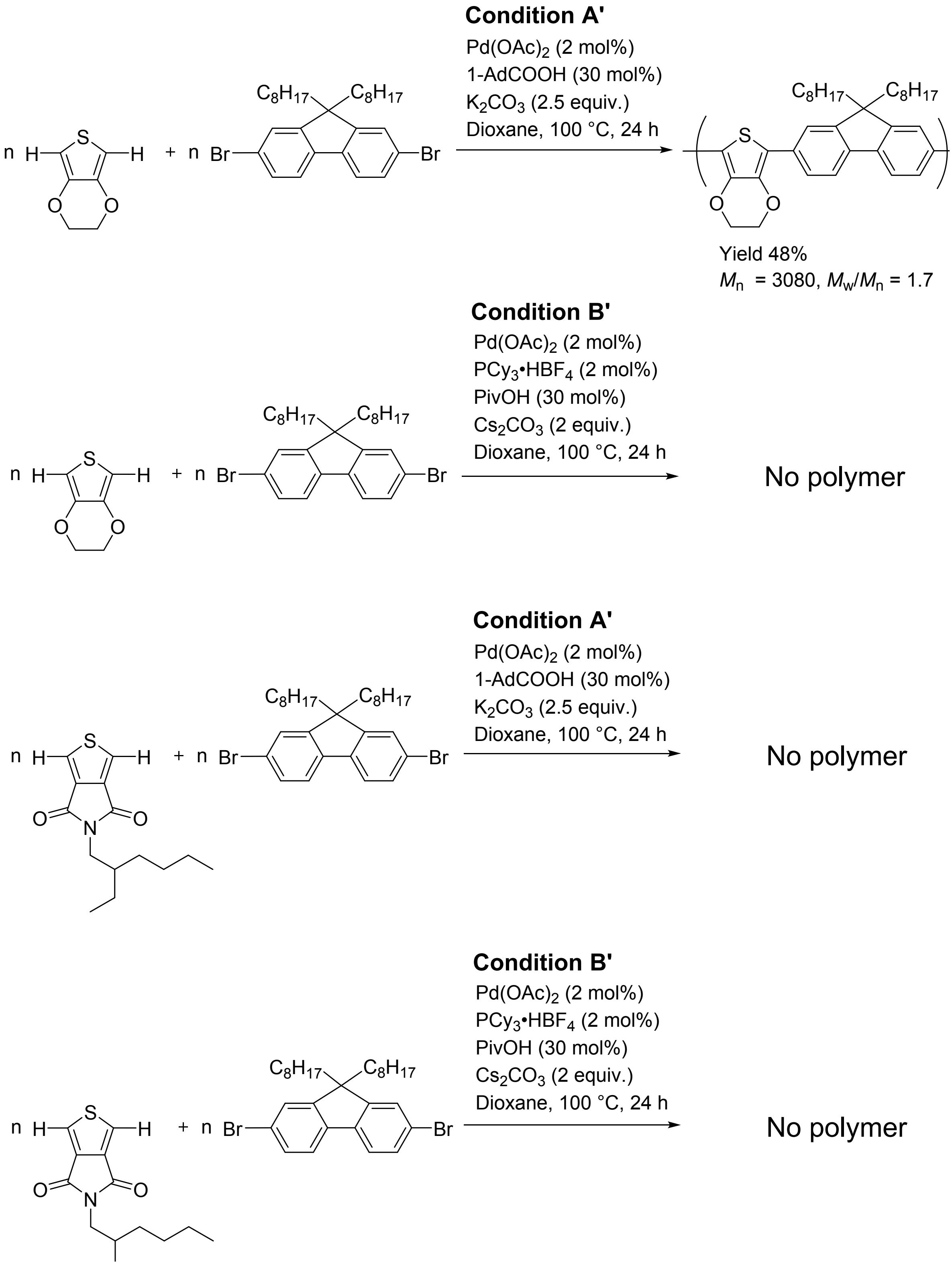
Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8573, Japan



Scheme S1



Scheme S2


Condition A'
Pd(OAc)$_2$ (2 mol%)
1-AdCOOH (30 mol%)
K$_2$CO$_3$ (2.5 equiv.)
Dioxane, 100 °C, 24 h
n
H
S
O
+ n
Br
C$_8$H$_{17}$
Yield 48%
M_n = 3080, M_w/M_n = 1.7
Condition B'
Pd(OAc)$_2$ (2 mol%)
PCy$_3$•HBF$_4$ (2 mol%)
PivOH (30 mol%)
Cs$_2$CO$_3$ (2 equiv.)
Dioxane, 100 °C, 24 h
No polymer
Condition A'
Pd(OAc)$_2$ (2 mol%)
1-AdCOOH (30 mol%)
K$_2$CO$_3$ (2.5 equiv.)
Dioxane, 100 °C, 24 h
N
No polymer
Condition B'
Pd(OAc)$_2$ (2 mol%)
PCy$_3$•HBF$_4$ (2 mol%)
PivOH (30 mol%)
Cs$_2$CO$_3$ (2 equiv.)
Dioxane, 100 °C, 24 h
No polymer

Scheme S3

Materials. 2,7-Dibromo-9,9-dioctylfluorene, 3,4-ethylenedioxythiophene, $Pd(OAc)_2$, K_2CO_3, and other chemicals were received from commercial suppliers and used without further purification. Anhydrous DMAc and toluene were purchased from Kanto Chemical and used as a dry solvent. *N*- (2-ethylhexyl)thieno[3,4-*c*]pyrrole-4,6-dione (TPD),[1] 3,4-dioctyloxythiophene,[2] 3,4-dimethylthiophene,[3] 3,4-dichlorothiophene,[4] and 3,4-dicyanothiophene[5] were prepared according to the literature methods.

General Methods. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AVANCE-400 and Bruker AVANCE-600 NMR spectrometers. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured with tetramethylsilane (TMS) as an internal standard. Gel permeation chromatography (GPC) measurements were carried out on a SHIMADZU prominence GPC system equipped with polystyrene gel columns, using $CHCl_3$ as an eluent after calibration with polystyrene standards. The high temperature GPC measurement on a TOSHO HLC-8121GPC/HT DF-8020 using *o*-dichlorobenzene as eluent at 140 °C after calibration with polystyrene standards. All manipulations for the reactions were carried out under nitrogen atmosphere using a standard Schlenk technique or a glovebox.

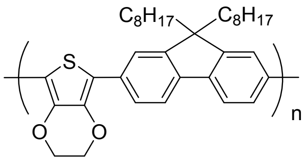
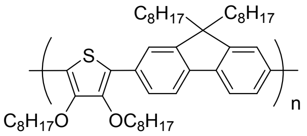
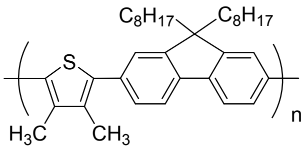
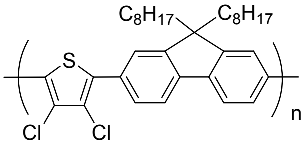
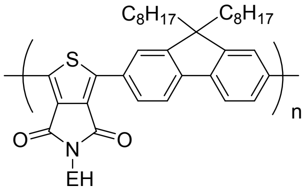
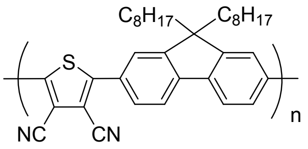
Synthesis of poly[(3,4-dioctyloxythiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)]. A mixture of $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), 1-adamantanecarboxylic acid (27 mg, 0.15 mmol), K_2CO_3 (173 mg, 1.25 mmol), 2,7-dibromo-9,9-dioctylfluorene (274 mg, 0.50 mmol), 3,4-dioctyloxythiophene (170 mg, 0.50 mmol) was stirred in anhydrous DMAc (1.7 mL) for 24 h at 100 °C under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into an aqueous solution of ethylenediaminetetraacetic acid disodium salt (pH = 8). The suspension was stirred overnight at room temperature. The precipitate was separated by filtration and washed with 0.1 M HCl solution, distilled water, and CH_3OH. The precipitate was dissolved in $CHCl_3$ and the solution was filtered through a plug of Celite to remove insoluble material. A reprecipitation from $CHCl_3/CH_3OH$ gave poly[(3,4-dioctyloxythiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] as yellow solid in 98% yield. $M_n = 11\ 300$, $M_w/M_n = 1.77$. ^1H NMR (600 MHz, $CDCl_3$): δ7.85 (s, 2H), 7.72 (overlapped, 4H), 4.10 (br, 4H), 2.07 (br, 4H), 1.79−1.82 (m, 4H), 1.09−1.48 (overlapped, 40H), 0.90 (t, J = 6.6 Hz, 6H), 0.81 (t, J = 7.2 Hz, 6H), 0.72 (br, 4H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 151.4, 146.8, 140.0, 132.1, 125.5, 124.2, 121.0, 119.8, 73.4, 55.3, 40.7, 31.9, 31.9, 30.5, 30.2, 29.6, 29.4, 29.4, 29.3, 26.2, 23.9, 22.7, 22.6, 14.1, 14.1.

Synthesis of poly[(3,4-dicyanothiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)]. A mixture of $Pd(OAc)_2$ (1.1 mg, 0.0050 mmol), $PCy_3 \cdot HBF_4$ (1.8 mg, 0.0050 mmol), pivalic acid (8.6 μL, 0.075 mmol), Cs_2CO_3 (163 mg, 0.50 mmol), 2,7-dibromo-9,9-dioctylfluorene (137 mg, 0.25 mmol), 3,4-dicyanothiophene (66 mg, 0.25 mmol) was stirred in anhydrous toluene (1.25 mL) for 24 h at 100 °C under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into an aqueous solution of ethylenediaminetetraacetic acid disodium salt (pH = 8). The suspension was stirred overnight at room temperature. The precipitate was separated by filtration and washed with 0.1 M HCl solution, distilled water, CH_3OH, and hexane. From the precipitate, the $CHCl_3$–soluble fraction was extracted with $CHCl_3$ and the solution was filtered through a plug of Celite. A reprecipitation from $CHCl_3/CH_3OH$ gave poly[(3,4-dicyanothiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] as yellow solid in 54% yield. $M_n = 32\ 500$, $M_w/M_n = 5.91$. ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, $J = 8.0$ Hz, 2H), 7.86 (overlapped, 4H), 2.13 (br, 4H), 1.18−1.12 (br, 20H), 0.81 (t, $J = 7.2$ Hz, 6H), 0.74 (br, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.2, 152.9, 142.5, 129.4, 127.1, 122.2, 121.5, 113.2, 108.6, 56.2, 40.1, 31.8, 29.9, 29.9, 29.2, 24.0, 22.6, 14.1.

Synthesis of poly[(3,4-dichlorothiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] (Condition B). A mixture of $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), $PCy_3 \cdot HBF_4$ (3.7 mg, 0.010 mmol), pivalic acid (17 µL, 0.15 mmol), Cs_2CO_3 (326 mg, 1.0 mmol), 2,7-dibromo-9,9-dioctylfluorene (274 mg, 0.50 mmol), 3,4-dichlorothiophene (77 mg, 0.50 mmol) was stirred in anhydrous toluene (2.5 mL) for 3 h at 100 °C under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into an aqueous solution of ethylenediaminetetraacetic acid disodium salt (pH = 8). The suspension was stirred 2 h at room temperature. The precipitate was separated by filtration and washed with 0.1 M HCl solution, distilled water, CH_3OH, and hexane. From the precipitate, the $CHCl_3$-soluble fraction was extracted with hot $CHCl_3$ and the solution was filtered through a plug of Celite. A reprecipitation from $CHCl_3/CH_3OH$ gave poly[(3,4-dichlorothiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] as yellow solid in 55% yield. $M_n = 8\ 300$, $M_w/M_n = 4.74$. ^1H NMR (600 MHz, $CDCl_3$): 7.83 (d, $J = 7.8$ Hz, 2H), 7.76 (s, 2H), 7.72 (d, $J = 7.8$ Hz, 2H), 2.06 (br, 4H), 1.11−1.22 (m, 20H), 0.82 (overlapped, 10H), $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.9, 141.0, 135.6, 131.1 127.6, 123.2, 121.5, 120.3, 55.6, 40.2, 31.8, 30.0, 29.2, 24.0, 22.6, 14.1.

Synthesis of poly[(3,4-dichlorothiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] (Condition A). A mixture of $Pd(OAc)_2$ (1.1 mg, 0.0050 mmol), 1-adamantanecarboxylic acid (14 mg, 0.075 mmol), K_2CO_3 (86 mg, 0.63 mmol), 2,7-dibromo-9,9-dioctylfluorene (137 mg, 0.25 mmol), 3,4-dichlorothiophene (38 mg, 0.25 mmol) was stirred in anhydrous DMAc (0.84 mL) for 3 h at 100 °C under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into an aqueous solution of ethylenediaminetetraacetic acid disodium salt (pH = 8). The suspension was stirred overnight at room temperature. The precipitate was separated by filtration and washed with 0.1 M HCl solution, distilled water, CH_3OH, and hexane. The precipitate was dissolved in $CHCl_3$ and the solution was filtered through a plug of Celite to remove insoluble material. A reprecipitation from $CHCl_3/CH_3OH$ gave poly[(3,4-dichlorothiophene -2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] as yellow solid in 72% yield. $M_n = 7\ 000$, $M_w/M_n = 2.29$. The NMR data are essentially same as those of the polymer obtained under condition B.

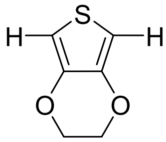
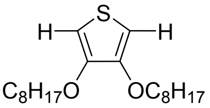
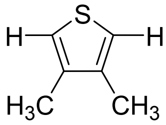
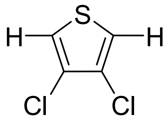
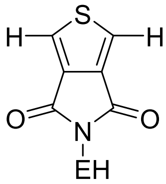
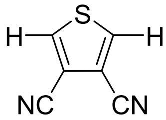
Table S1 Solubility of the obtained polymers

	$CHCl_3$	Toluene	THF	DMAc
 M_n = 43000, M_w/M_n = 2.7	S	S	S	PS PS*
 M_n = 11000, M_w/M_n = 1.8	S	S	S	I PS*
 M_n = 14000, M_w/M_n = 2.4	S	S	PS S*	I PS*
 M_n = 8300, M_w/M_n = 4.7	PS S*	PS S*	PS PS*	I PS*
 M_n = 46300, M_w/M_n = 1.9	S	S	S	I PS*
 M_n = 33000, M_w/M_n = 5.9	PS S*	I PS*	PS S*	I PS*

The solubility tests were conducted at 1 mg/mL at room temperature.

S: Soluble, PS: Partly soluble, I: Insoluble. *Solubility at boiling temperature for $CHCl_3$ and THF, and at 100 °C for toluene and DMAc.

Table S2 Hammett substituent constants and chemical shift of the methine carbon of the monomers

Entry	Monomer	Model substituent	σ_p[a]	σ_m[a]	^{13}C NMR / ppm [b]
1		$-OCH_3$	-0.27	0.12	99.6
2		$-OCH_3$	-0.27	0.12	96.8
3		$-CH_3$	-0.17	-0.07	120.7
4		-Cl	0.23	0.37	125.0
5		$-CONH_2$	0.36	0.28	125.4
6		-CN	0.66	0.56	136.9

[a] Hammett substituent constants of the model substituents, reference 6. [b] Chemical shift of the methine carbon of the monomer in $CDCl_3$.

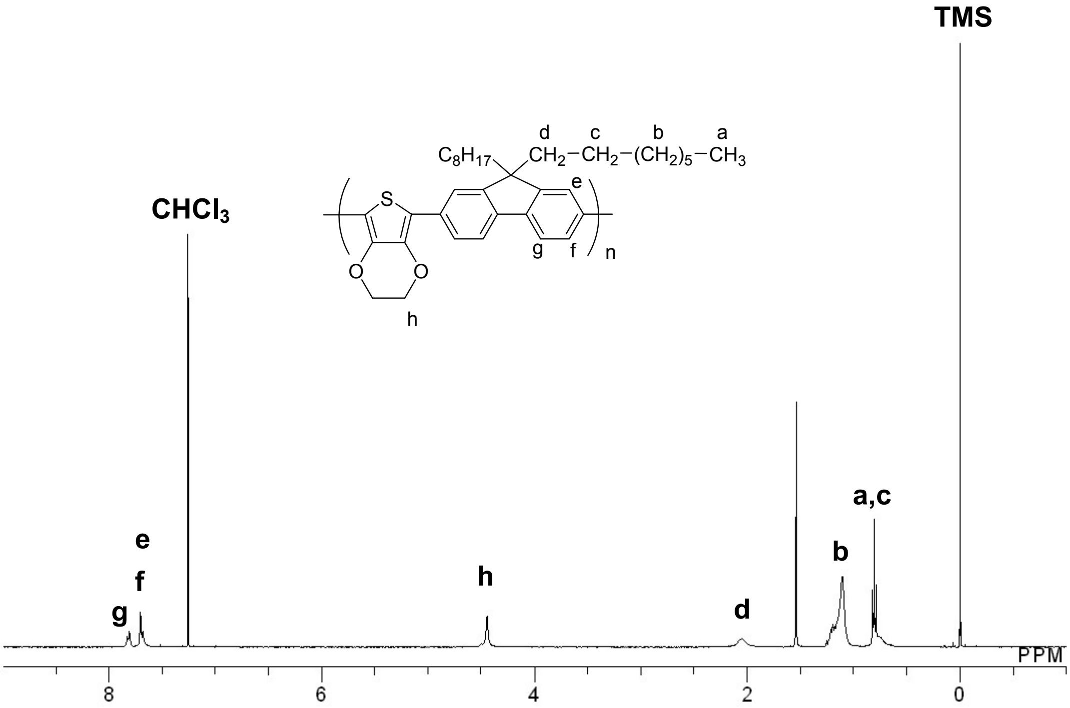


Figure S1 ^{1}H NMR spectrum of poly[(3,4-ethylenedioxythiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] (400 MHz, CDCl$_3$).

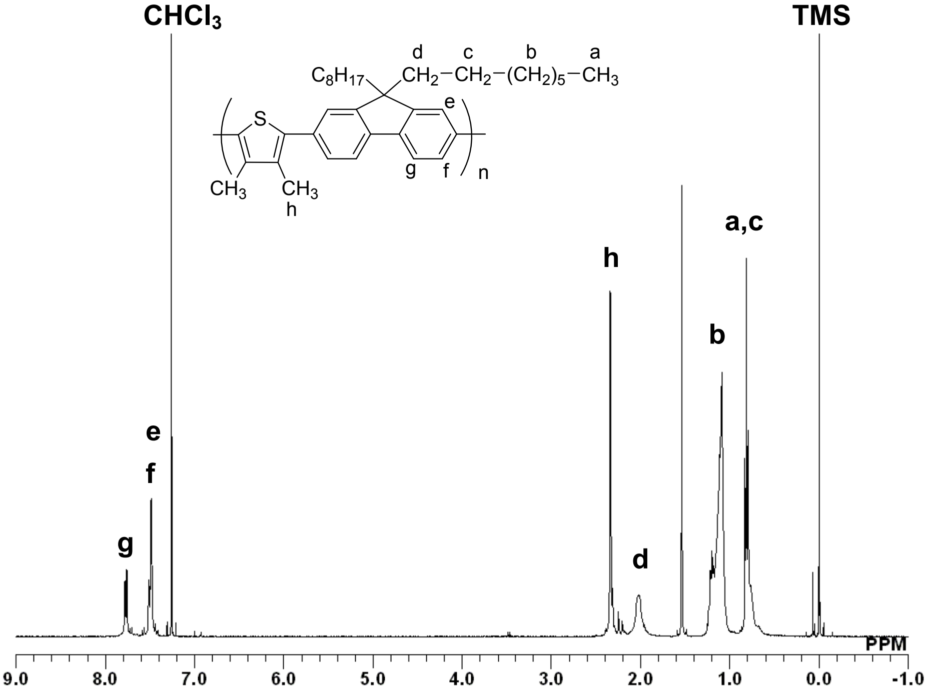


Figure S2 ^{1}H NMR spectrum of poly[(3,4-dimethylthiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] (400 MHz, CDCl$_3$).

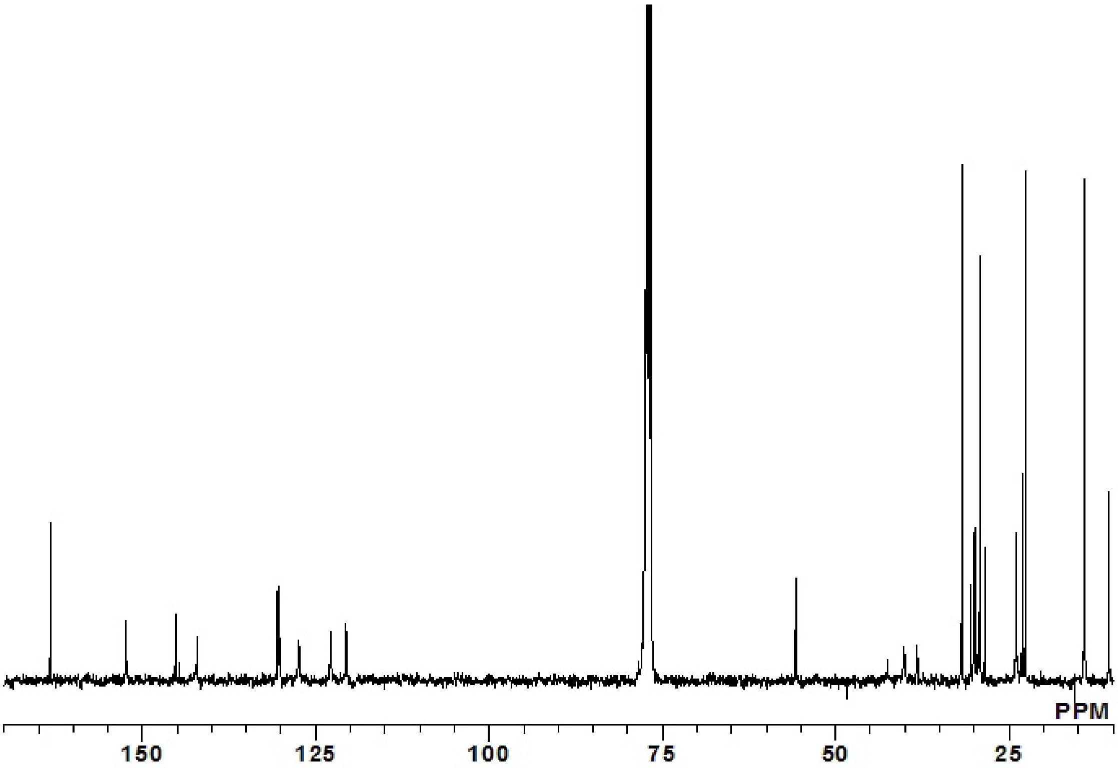


Figure S3 $^{13}C\{^1H\}$ NMR spectrum of **PTPDF** (100 MHz, $CDCl_3$).

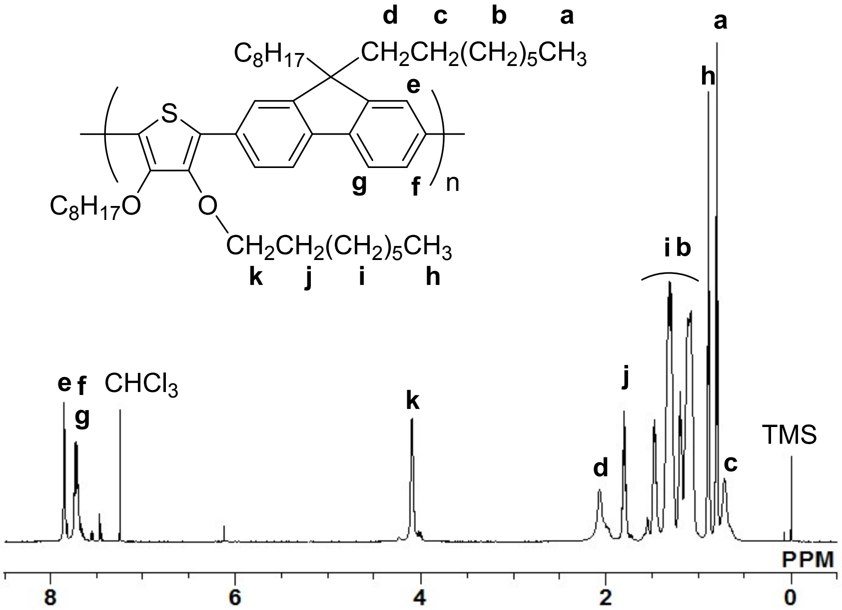


Figure S4 ^1H NMR spectrum of poly[(3,4-dioctyloxythiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] (600 MHz, $CDCl_3$).

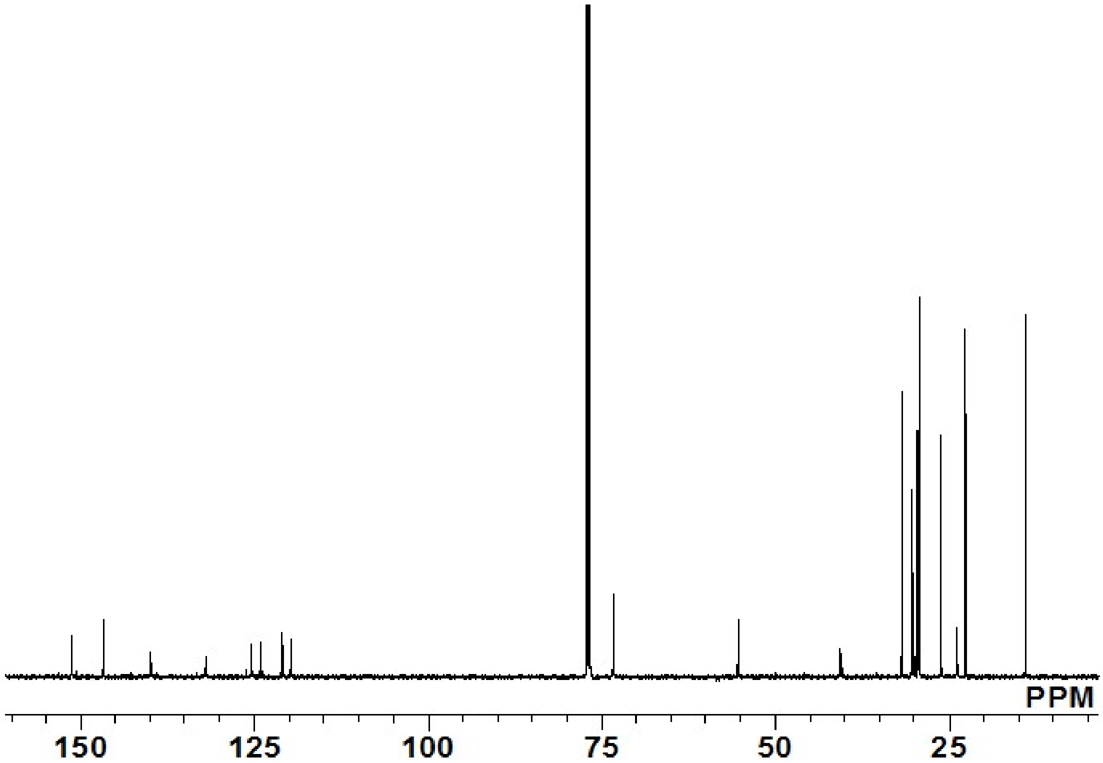


Figure S5 $^{13}C\{^1H\}$ NMR spectrum of poly[(3,4-dioctyloxythiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] (150 MHz, $CDCl_3$).

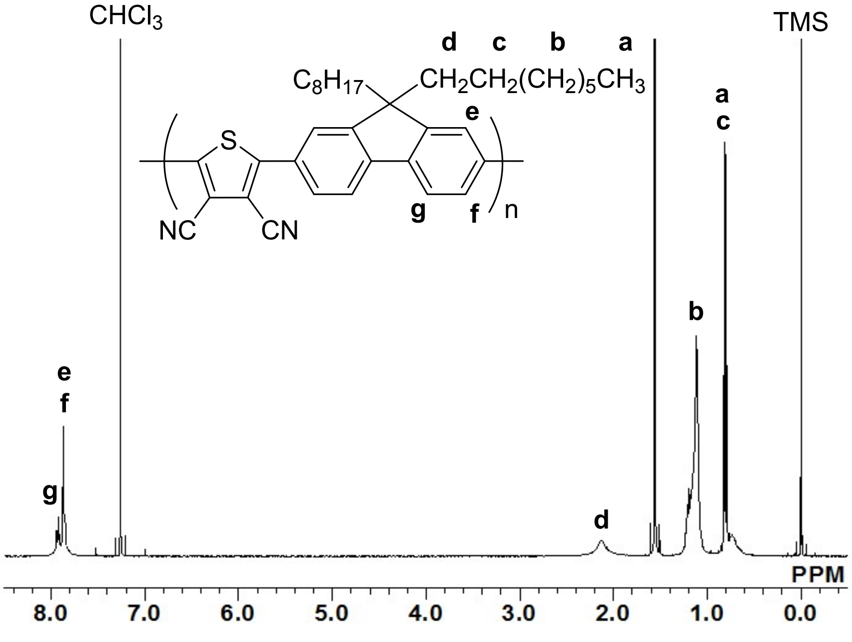


Figure S6 ^1H NMR spectrum of poly[(3,4-dicyanothiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] (400 MHz, $CDCl_3$).

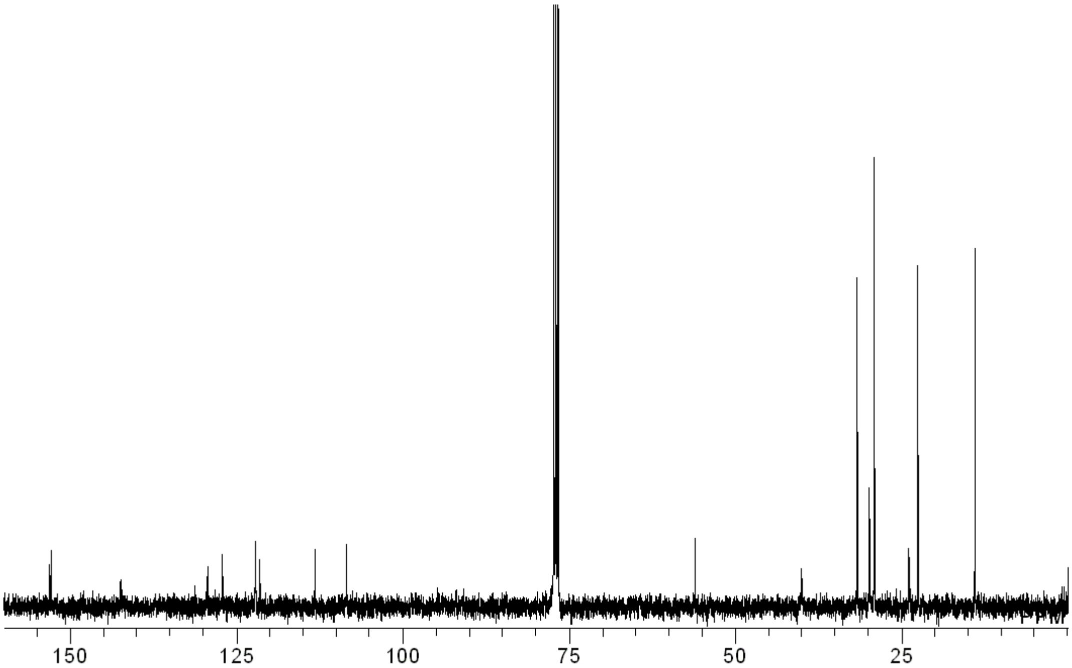


Figure S7 $^{13}C\{^1H\}$ NMR spectrum of poly[(3,4-dicyanothiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] (100 MHz, $CDCl_3$).

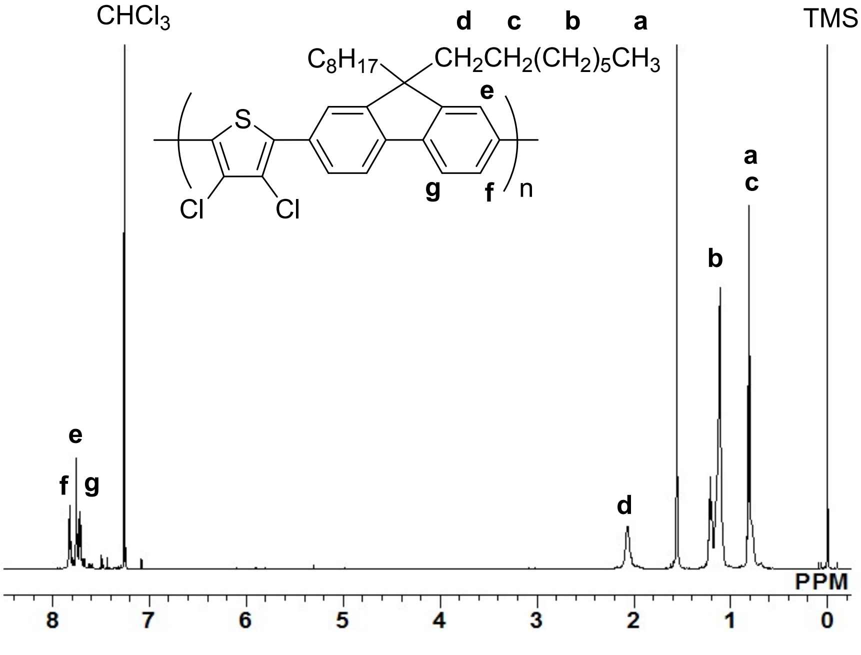


Figure S8 ^1H NMR spectrum of poly[(3,4-dichlorothiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] (600 MHz, $CDCl_3$).

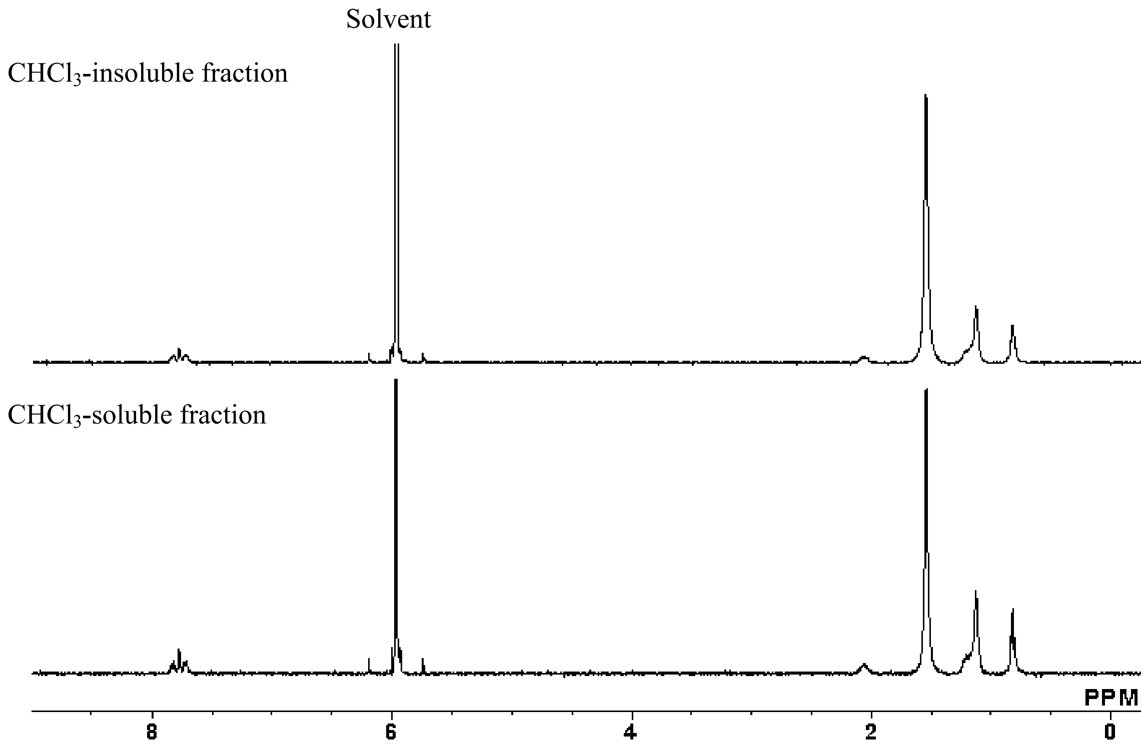


Figure S9 ^{1}H NMR spectra of a CHCl$_3$-insoluble fraction an a CHCl$_3$-soluble fraction of poly[(3,4-dichlorothiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] (400 MHz, CD$_2$Cl$_4$ at 333 K).

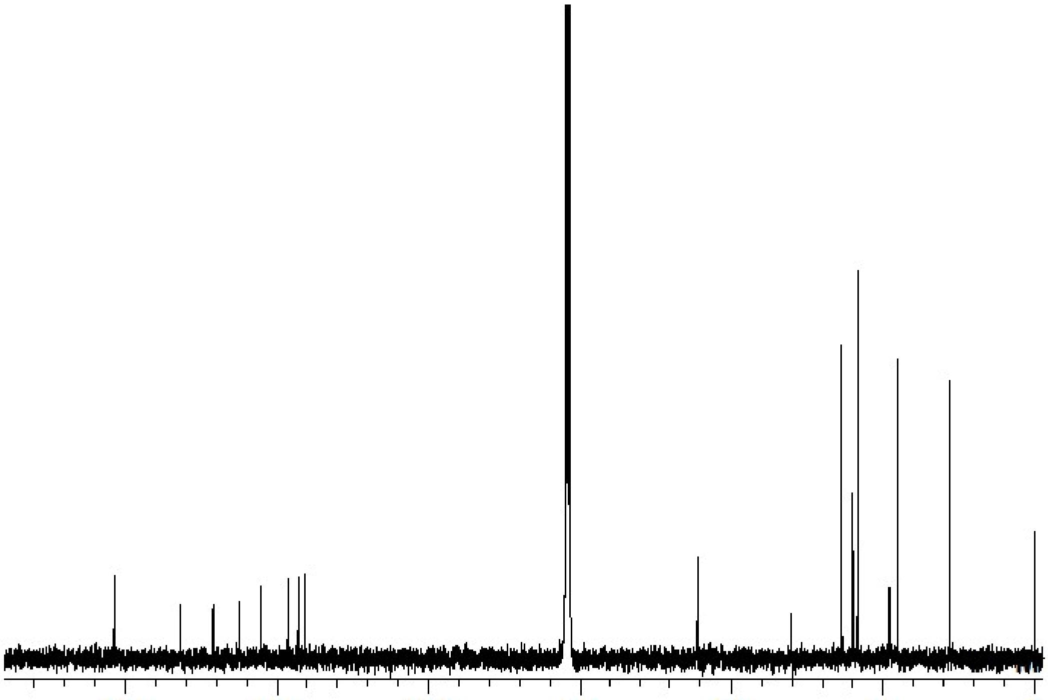


Figure S10 ^{13}C{^{1}H} NMR spectrum of poly[(3,4-dichlorothiophene-2,5-diyl)-(9,9-dioctylfluorene-2,7-diyl)] (100 MHz, CDCl$_3$).

References

1 (a) C. B. Nielsen and T. Bjørnholm, *Org. Lett.,* 2004, **6**, 3381; (b) C. Piliego, T. W. Holcombe, J. D. Douglas, C. H. Woo, P. M. Beaujuge and A. M. Fréchet, *J. Am. Chem. Soc*., 2010, **132**, 7595.

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4 A. Henckens, M. Knipper, I. Polec, J. Manca, L. Lutsen and D. Vanderzande, *Thin Solid Films,* 2004, **451-452**, 572.

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