Electronic Supplementary Information for

Kumada Catalyst Transfer Polycondensation for Controlled Synthesis of Polyfluorenes Using 1,3-Bis(diarylphosphino)propanes as Ligands

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Experimental section

Measurements

^{1}H NMR spectra were recorded on a BrukerAV400 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal reference.^{31}P NMR (162 MHz) spectra were measured using $CDCl_3$, C_6D_6 or THF as solvent and H_3PO_4 as an outer standard. GC−MS measurements were performed on an Agilent 5975/6890N, which was equipped with an Agilent HP-5 column (30 m). The internal reference was 1,4-dihexyloxybenzene or 1,4-dioctyloxybenzeneused. The M_ns and PDIs of polymers were measured with a Waters 2414 system equipped with Waters HT4 and HT3 column-assembly and a Waters 2414 refractive index detector using THF as eluent (flow rate: 1.00 mL/min) and polystyrene as standard at 40 °C. MALDI−TOF mass spectra were recorded on a Kompact MALDI Mass Spectrometer in a linear mode with anthracene-1,8,9-triol as matrix.

Materials

THF was dried over sodium and distilled from sodium-benzophenone before used. Isopropylmagnesium chloride (^{i}PrMgCl, 2.0 M solution in THF) and LiCl were purchased from Acros. $Ni(acac)_2$ (95%) was purchased from Aladdin and used directly without further purification. The ligand dppp was bought from Pacific Chem Source, Inc. and recrystallized from alcohol. 2-Bromo-7-iodo-9,9-dioctylfluorene, 2-bromo-5-iodo-3-hexylthiophene, 1,4-dihexyloxybenzene and 1,4-dioctyloxybenzene were synthesized according to literature.[1-3]

Synthesis of ligands L1, L2 and L3

Bis(4-methylphenyl)-phosphine oxide (1a). Into a dried 250 mL Schlenk flask containing Mg (1.02 g, 42.10 mmol) and THF (100 mL) was added a diethyl ether (Et_2O, 20 mL) solution of *p*-bromotoluene (6.00g, 35.08 mmol) dropwise at ambient temperature. The resulting mixture was refluxed for 2 hours with stirring. Then, diethylphosphite (1.51 mL, 11.69 mmol) was added via a syringe to the solution, and stirred at 25 ^{o}C overnight. Aqueous ammonium chloride solution was introduced to the solution. The mixture was extracted with Et_2O. The organic phase was washed

with sodium thiosulfate ($Na_2S_2O_3$) and sodium carbonate (Na_2CO_3) aqueous solutions and then brine. The organic extracts were dried with anhydrous magnesium sulfate (Mg_2SO_4). After the solvent was evaporated at reduced pressure, the crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (1/1, v/v) as eluent to afford **1a** as a white powder in a yield of 91% (2.30 g). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) 8.03 (d, J = 636 Hz, 1H), 7.61-7.54 (m, 4H), 7.61-7.54 (m, 4H), 7.30-7.27 (m，4H), 2.39 (s, 6H). ^{31}P NMR(162 MHz, $CDCl_3$) δ(ppm) 21.52(s).

Bis(3-methylphenyl)-phosphine oxide (1b). The procedure identical to the preparation of **1a** was employed for the synthesis of **1b** in a yield of 87% (2.00 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (d, 1 H，J= 636Hz)，7.63-7.58 (m, 4H)，7.00-6.98 (m, 4H)，3.85 (s, 6H). ^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) 20.55 (s).

Bis-(2-methylphenyl)-phosphine oxide (1c). The procedure identical to the preparation of **1a** was employed for the synthesis of **1c** in a yield of 88% (2.03 g). ^{1}H NMR(400 MHz, $CDCl_3$) δ (ppm) 8.21(d, 1H，J= 381 Hz), 7.71(dd, 2H, J = 12.2，5.9Hz), 7.47(t, 2H, J= 6Hz), 7.33(t, 2H, J= 7.5 Hz), 7.25(dd, 2H, J= 9.9, 5.7Hz), 2.38(s，6H). ^{31}P NMR (162 MHz, $CDCl_3$) δ(ppm) 17.82 (s).

1,3-Bis(di(4-methylphenyl)phosphinyl)propane (2a). Into a solution of **1a** (1.83 g, 7.95 mmol) in THF (20 mL) was added NaH (0.32 g, 7.95 mmol). After stirred for 30 minutes, 1,3-dibromopropane was introduced and the mixture was stirred for 4 hours at room temperature. The reaction mixture was quenched with water for extraction with Et_2O. The organic extracts were washed with brine and dried with $MgSO_4$. After solvent was evaporated at reduced pressure, the crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10/1,v/v) as eluent to afford **2a** as a white powder in a yield of 95% (1.89 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.59-7.50 (m，8H), 7.25-7.18 (m, 8H), 2.47-2.36 (m，4H), 2.37(s，12H), 2.04-1.86 (m，2H). ^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) 33.32 (s).

1,3-Bis(di(3-methylphenyl)phosphinyl)propane (2b). The procedure identical to the preparation of **2a** was employed for the synthesis of **2b** in a yield of 92% (1.84 g).

^{1}H NMR(400 MHz, $CDCl_3$) δ (ppm) 7.35-7.31 (m，4H), 7.29-7.25(m，4H), 7.23-7.18 (m, 4H), 7.05-6.97(m, 4H), 3.80(s, 12H), 2.52-2.40 (m, 4H)，2.09-1.95 (m, 2H). ^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) 32.34(s).

1,3-Bis(di(2-methylphenyl)phosphinyl)propane (2c). The procedure identical to the preparation of **2a** was employed for the synthesis of **2c** in a yield of 91% (1.82 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.63-7.53 (m，8H), 6.97-6.87(m, 8H), 2.47-2.36(m，4H), 3.83(s，12H), 2.45-2.34(m，4H), 2.02-1.89(m，2H). ^{31}P NMR(162 MHz, $CDCl_3$) δ(ppm) 32.25(s).

1,3-Bis(di(4-methylphenyl)phosphino)propane (L1). Into a refluxed solution of **2a** (1.53 g, 3.06 mmol) and di(*p*-nitrophenyl) phosphoric acid (0.31 g, 24.45 mmol) in toluene (40 mL) was added diethoxymethylsilane (3.28 g, 0.92 mmol) dropwise. The resulting mixture was stirred for additional 36 hours, and then cooled to 0 ^{o}C. Then, KOH in methanol (15 mL, 3 mol/L, 45 mmol) was added slowly. After stirred for 3 hours, the mixture was poured into water for extraction with ethyl acetate. The organic extracts were washed with brine and dried with $MgSO_4$. After solvent was evaporated at reduced pressure, the crude product was purified by column chromatography on silica gel with ethyl acetate as eluent to afford L1 as a white powder in a yield of 81% (1.16 g). ^{1}H NMR (400 MHz, C_6D_6) δ (ppm) 7.38 (t, 8H, J= 8Hz), 6.93 (d, 8H, J= 8Hz), 2.14(t, 4H, J= 8Hz), 2.05 (s，12H), 1.82-1.70 (m，2 H). ^{31}P NMR (162 MHz, C_6D_6) δ (ppm) -6.26 (s).

1,3-Bis(di(3-methylphenyl)phosphino)propane (L2). The procedure identical to the preparation of L1 was employed for the synthesis of L2 in a yield of 68% (0.82 g). ^{1}H NMR (400 MHz, C_6D_6) δ (ppm) 7.38-7.28 (m, 8H)，7.03-6.88 (m, 8H), 2.32 (s, 12H), 2.12-2.04 (m, 4H), 1.76-1.64 (m，2 H). ^{31}P NMR (162 MHz, C_6D_6) δ (ppm) -4.70 (s).

1,3-Bis(di(3-methylphenyl)phosphino)propane (L3). The procedure identical to the preparation of L1 was employed for the synthesis of L3 in a yield of 78% (0.94 g). ^{1}H NMR (400 MHz, C_6D_6) δ (ppm) 7.25-7.20 (m, 4H), 7.08-6.93 (m, 12H), 2.38 (s, 12H), 2.05-1.98 (m，4H), 1.74-1.60 (m，2 H). ^{31}P NMR (162 MHz, C_6D_6) δ (ppm)

-26.06 (s).

Preparation of the catalyst Ni(acac)$_2$/L with Ni(acac)$_2$/dppp as an example. A solution of Ni(acac)$_2$ (20.6 mg, 0.08 mmol) and 1,3-bis(diaryllphosphino)propane (33.7 mg, 0.0816 mmol) in THF (2 mL) was stirred at room temperature for 20 minutes before use.

Preparation of M1. Into a mixture of 2-bromo-7-iodo-9,9-dioctylfluorene (594.4 mg, 1.0 mmol), 1,4-dihexyloxybenzene (0.139g 0.5 mmol), LiCl (42.4 mg, 1.0 mmol) and THF (20 mL) was added ^{i}PrMgCl (2.0 mol/L in THF, 0.5 mL, 1.0 mmol) at -20 ^{o}C in argon atmosphere. The mixture was stirred for 1 hour and ready for use. The conversion of 2-bromo-7-iodo-9,9-dioctylfluorene was 94.0% as determined by GC-MS.

Preparation of M2. Into a mixture of 2-bromo-5-iodo-3-hexylthiophene (186.5 mg, 0.5 mmol), 1,4-dioctyloxybenzene (83.6mg 0.25 mmol), LiCl (21.2mg, 0.50 mmol) and THF (16 mL) was added ^{i}PrMgCl (2.0 mol/L in THF, 0.25 mL, 0.50 mmol) dropwise at -20 ^{o}C in argon atmosphere. The reaction mixture was stirred for 1 hour. The conversion of 2-bromo-5-iodo-3-hexylthiophene was 96.5% as determined by GC-MS.

General polymerization procedure with 0.5 mol % Ni(acac)$_2$/dppp as an example. Into a THF solution of M1 as prepared above was added Ni(acac)$_2$/dppp (0.125 mL, 0.005 mmol) in THF at 0 ^{o}C. The resulting mixture was stirred at 0 ^{o}C for 2 hours, and then quenched by adding 5 mol/L aqueous HCl. The mixture was extracted with $CHCl_3$, and the organic extracts were washed with brine and dried with $MgSO_4$. The solution was concentrated to about 5 mL, and then precipitated into methanol. The precipitation was collected by filtration and then dried in vacuum to afford the polymer in a yield of 70% (272 mg). M_n = 80.0 kDa, PDI = 1.56. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86-7.83 (br, 2 H), 7.72-7.68 (br, 4 H), 2.24-1.90 (br, 4 H), 1.29-0.99 (m, 20 H), 0.82 (t, J = 8 Hz, 10H).

Polymerization kinetics with 1 mol % Ni(acac)$_2$/L2 as an example. Into a THF solution of M1 as prepared above was added Ni(acac)$_2$/L2 (0.125 mL, 0.005 mmol) in

THF at 0 ^{o}C. The polymerization solution (2 mL) was taken out at 0.5, 2, 5.5, 10, 15 and 20 min, respectively. The solutions were quenched and extracted with $CHCl_3$ for measuring conversion and molecular weight at different polymerization time.

Synthesis of block polymers with P7 as an example. Into a solution of M1 (10 mL, 0.50 mmol) was added $Ni(acac)_2$/dppp (0.125 mL, 0.005 mmol) in THF at 0 ^{o}C. After 10 minutes, the solution of M2 was added, and the mixture was stirred for another 1 hour and then quenched by adding 5 mol/L aqueous HCl for extraction with $CHCl_3$. The organic extracts were washed with brine and dried with $MgSO_4$. The solution was concentrated to about 5 mL, and then precipitated in methanol. The precipitation was collected by filtration and dried in vacuum to afford **P7** in a yield of 69% (191 mg).

References

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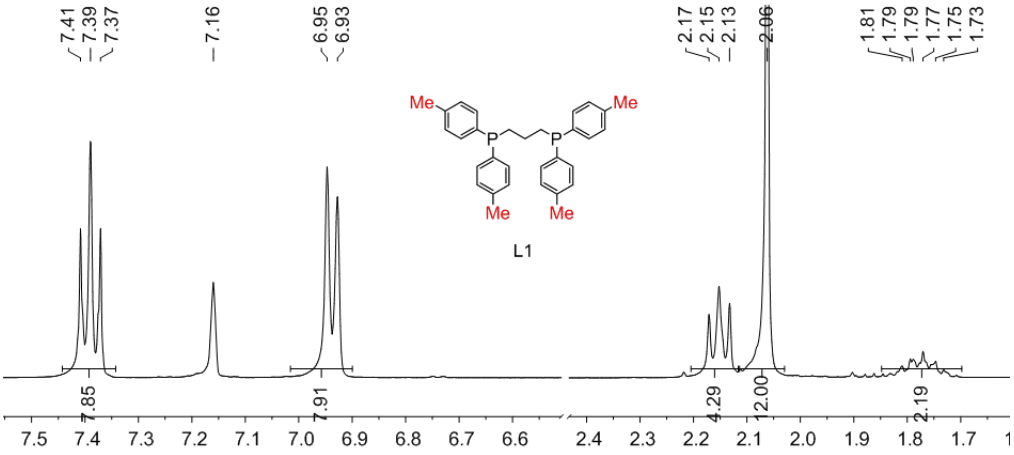

Fig. S1 ^{1}H NMR spectrum of L1.

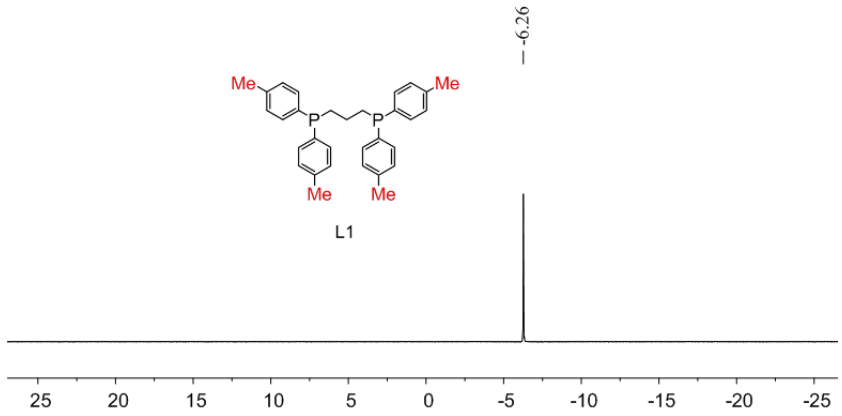

Fig. S2 ^{31}P NMR spectrum of L1.

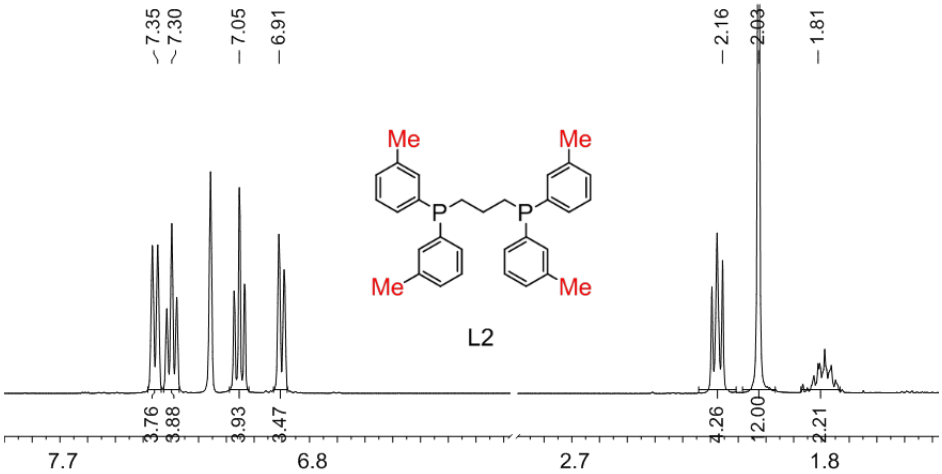

Fig. S3 ^{1}H NMR spectrum of L2.

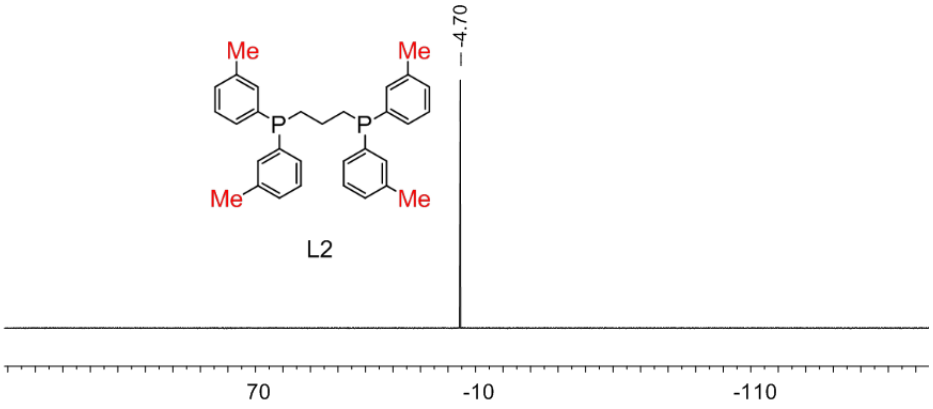

Fig. S4 ^{31}P NMR spectrum of L2.

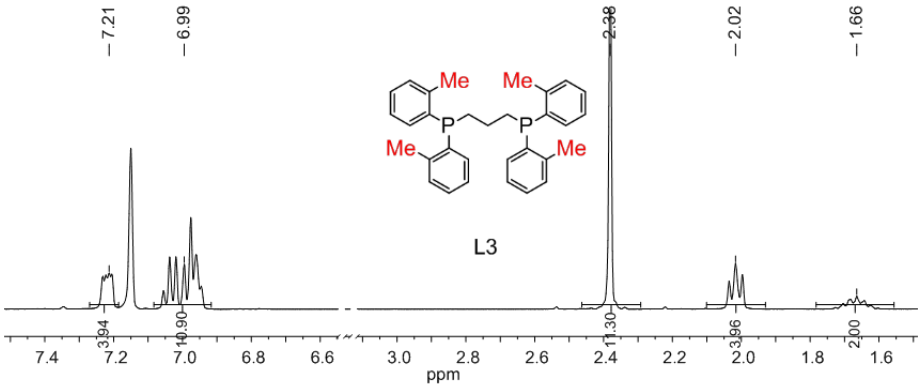

Fig. S5 ^{1}H NMR spectrum of L3.

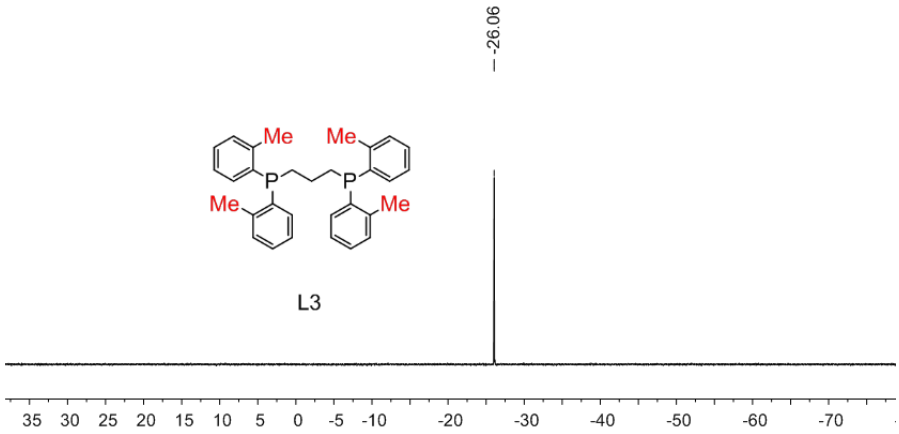

Fig. S6 ^{31}P NMR spectrum of L3.

Table S1. The polymerization results with different amount of $Ni(acac)_2$/dppp as catalyst.[a]

Entry	[Ni]/[M1]$_0$(mol%)	M_n[b](kDa)	PDI[b]	Yield[c](%)
1	10	2.8	1.24	55
2	6	8.9	1.17	79
3	4	14.1	1.22	74
4	2	29.5	1.22	76
5	1	62.2	1.23	80
6[d]	0.5	80.0	1.56	70

[a]All polymerizations were carried out at 0 ^oC for 1 h in the presence of 1 equiv. LiCl with $[M1]_0$ = 0.05mol/L. [b]Estimated by GPC with polystyrene as the standard and THF as eluent. [c]Yield after precipitation. [d]Polymerization for 2 h.

Table S2. The polymerization results with different amount of $Ni(acac)_2$/L1 as catalyst.[a]

Entry	[Ni]/[M1]$_0$(mol%)	M_n[b](kDa)	PDI[b]	Yield[c](%)
1	10	2.8	1.25	76
2	6	6.5	1.21	82
3	4	11.2	1.22	82
4	2	27.5	1.25	79
5	1	58.7	1.28	81
6[d]	0.5	78.4	1.38	74

[a]All polymerizations were carried out at 0 ^oC for 1 h in the presence of 1 equiv LiCl with $[M1]_0$ = 0.05mol/L. [b]Estimated by GPC with polystyrene as the standard and THF as eluent. [c]Yield after precipitation. [d]Polymerization for 2 h.

Table S3. The polymerization results with different amount of $Ni(acac)_2$/L3 as catalyst.[a]

Entry	[Ni]/[M1]$_0$(mol%)	M_n[b](kDa)	PDI[b]	Yield[c](%)
1	10	3.7	1.26	71
2	6	8.7	1.34	72
3	4	15.8	1.70	78
4	2	22.8	1.73	73
5	1	25.3	1.85	76
6[d]	0.5	27.3	1.87	77

[a]All polymerizations were carried out at 0 ^oC for 1 h in the presence of 1 equiv LiCl with $[M1]_0$ = 0.05mol/L. [b]Estimated by GPC with polystyrene as the standard and THF as eluent. [c]Yield after precipitation. [d]Polymerization for 2 h.

Table S4. The polymerization results with different amount of $Ni(acac)_2$/L2 as catalyst.[a]

Entry	[Ni]/[M1]$_0$ (mol%)	M_n[b](kDa)	PDI[b]	Yield[c](%)
1	10	4.0	1.33	74
2	6	7.4	1.30	73
3	4	14.1	1.25	77
4	2	29.1	1.31	81
5	1	56.4	1.32	81
6[d]	0.67	76.1	1.37	79
7[d]	0.5	91.1	1.44	82
8[d]	0.33	101.0	1.70	76

[a]All polymerizations were carried out at 0 ^oC for 1 h in the presence of 1 equiv LiCl with $[M1]_0$ = 0.05mol/L. [b]Estimated by GPC with polystyrene as the standard and THF as eluent. [c]Yield after precipitation. [d]Polymerization for 2 h.

Table S5. Synthesis of PF8-*b*-P3HTs with $Ni(acac)_2$/L2 as the catalyst.[a]

Entry	$[Ni]/[M1]_0$ (mol%)	t[b] (min)	$[M1]_0/[M2]_0$	PF8		PF8-*b*-P3HT			Yield (%)[d]
				M_n (kDa)[c]	PDI[c]	Polymer	M_n (kDa)[c]	PDI[c]	
1	4	5	1:4	13.4	1.17	**P13**	36.4	1.21	73
2	2	8	1:2	28.8	1.22	**P14**	51.7	1.25	70
3	1	10	1:1	55.1	1.29	**P15**	78.4	1.36	75

[a]All polymerizations were carried out in the presence of 1 equiv LiCl at 0 °C for M1 and room temperature for M2 and was polymerized for 1 h except **P15** for 2h. [b]The intial polymerization time for M1. [c]Estimated by GPC with polystyrene as the standard and THF as eluent. [d]Yield after precipitation.

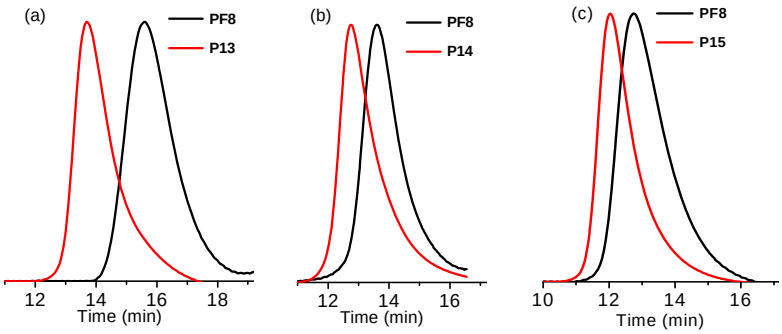

Fig. S7. The GPC curves of PF8-*b*-P3HTs with $Ni(acac)_2$/L2 as the catalyst (a) **P13**; (b) **P14**; (c) **P15**.

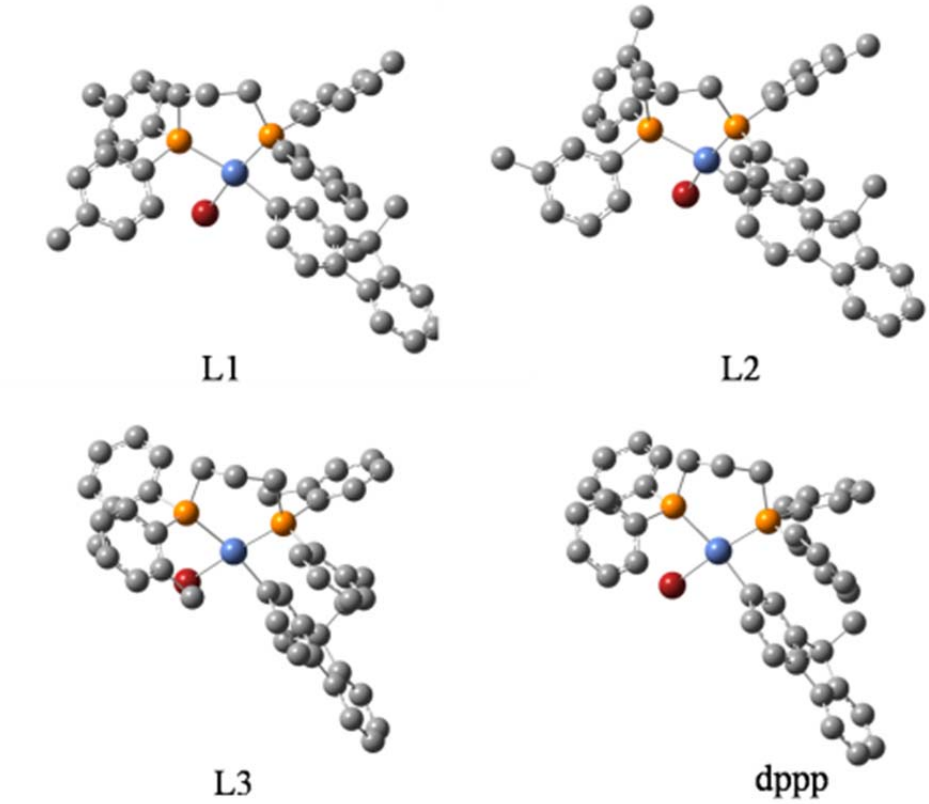

Fig. S8 Optimized structures of fluorine-LNiBr