***Electronic Supplementary Information* for**

Controlled Synthesis of High Molecular Weight Poly(3-hexylthiophene)s via Kumada Catalyst Transfer Polycondensation with Ni(IPr)(acac)₂ as the Catalyst

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General information

^{1}H NMR spectra were obtained on a Bruker 400 MHz spectrometer with $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal reference. The conversions of monomer were determined by gas chromatography (GC) on a SHIMADZU GC-14C instrument equipped with an OV-1701 column with 1,4-dihexyloxybenzene as internal reference. Samples were injected in a split mode with a ratio of 30:1 and an injector temperature of 280 °C. The column temperature was programmed as follows: 100 °C held for 3 min, increased to 280 °C at 10 °C min^{-1} and then held for 5 min. The FID temperature was set to 300 °C. Gel permeation chromatography (GPC) analysis was performed at 150 °C on a Polymer Laboratories Ltd. GPC 220 instrument with 1,2,4-tirchlorobenzene as eluent (0.05% 2,6-di-tert-butyl-4-methylphenol stabilized, flow rate: 1.0 mL/min, standard: polystyrene). Static light scattering (L= 658 nm) measurement was performed on the same equipment but equipped with triple detectors (PD 2040 high temperature light scattering detector, PL-BV 400 HT viscometer and refrative index detector). The polymer solutions were filtered through Acrodisc 0.45 μm poly(tetrafluoroethylene) filter prior to the measurements. The average refractive index increment (d*n/dc)* of P3HT in 1,2,4-tirchlorobenzene at 150 °C is 0.111 mL/g. Single crystal data collection was carried out with graphite monochromated MoKα radiation (λ = 0.71073 Å) on a Bruker Smart APEX diffratometer with a charge-coupled device (CCD) detector and graphite monochromator. The intensity data were collected in the ω scan mode (186 K), and absorption corrections were performed using the SADABS program.[1] Data reduction was performed using SAINT and corrected for Lorentz and polarization effects. The crystal structure was solved using the SHELXTL program and refined using full matrix least squares.[2] The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with the attached carbon atoms. Density Functional theory (DFT) calculations were carried out using the Amsterdam Density Functional (ADF) program package.[3] All the structures and energies

were calculated based on the Becke-Perdew exchange-correlation functional.[4,5] A triple STO basis set was employed for Ni, while all other atoms were described by a double-ζ plus polarization STO basis. The 1s electrons of C and N atoms, the 1s-2p electrons of S, P, Ni atoms and the 1s-3p electrons of Br atom were treated as frozen core.

Materials.

Tetrahydrofuran (THF) and toluene was dried with sodium-benzophenone and distilled. Nickel acetylacetonate ($Ni(acac)_2$, 95%) was purchased from Aladdin. Lithium chloride (LiCl) and isopropylmagnesium chloride (^iPrMgCl, 2.0 M solution in THF) were bought from Acros. Bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (IPr) and $Ni(IPr)(acac)_2$ were prepared following literature procedures.[6,7] $Ni(IPr)(acac)_2$ was purified by recrystallization from THF at -35 ºC. Single-crystals of $Ni(IPr)(acac)_2$ were grown from C_6D_6 solution via the slow evaporation of solvent at room temperature. Anal. Calcd for $Ni(IPr)(acac)_2$: N, 4.26; C, 69.17; H, 8.07. The complex $Ni(dppp)Cl_2$ (98%) was bought from Pacific ChemSource, Inc. $Ni(dppp)(acac)_2$ was synthesized following our previous report and purified by recrystallization from hexane/toluene.[8]

General procedure for the polymerizations using $Ni(IPr)(acac)_2$ as the catalyst:

Preparation of 2-bromo-5-chloromagnesio-3-hexylthiophene (1) solution in THF (0.10 mol/L).

2-Bromo-5-iodine-3-hexylthiophene (1.865 g, 5 mmol), 1,4-dihexyloxybenzene (0.6950 g, 2.5 mmol), lithium chloride (0.210 g, 5 mmol) and dry THF (47.5 mL) were added into a 50 mL Schlenk flask under nitrogen atmosphere. Then ^iPrMgCl (1.931 M, 2.54 mL, 4.9 mmol) was added into the flask. The mixture was stirred at -20 ºC for 1 h, and then warmed to room temperature.

Polymerization with 0.50 mol % catalyst as an example. Into a 10 mL Schlenk flask was added solution of **1** (5 mL, 0.50 mmol) prepared as shown above. Then $Ni(IPr)(acac)_2$ (5 mmol/L in THF, 0.5 mL, 2.5 μmol) was added. The mixture was stirred at 25 ºC for 30 min, and then the polymerization was terminated by adding 2 mL aqueous HCl (5 mol/L). The mixture was poured

into petroleum ether (50 mL) and thoroughly stirred for 45 min. Petroleum ether solution (3 mL) was taken off and dried with $MgSO_4$ for GC measurement. The polymer was collected by filtration, washed with water and acetone in succession. The crude polymer was dissolved in 1,2-dichlorobenzene (4 mL), and then precipitated in methanol. The precipitation was collected by filtration and then dried in vacuum (73 mg, 88.7%). GPC data: M_n = 98.0 kg/mol, PDI = 1.21. ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C): 6.99 (s, 1 H), 2.83 (t, 2 H), 1.72 (m, 2 H), 1.47 (m, 2 H), 1.35 (m, 4 H), 0.91 (t, 3 H).

Polymerization kinetics

Polymerization with 0.15 mol % catalyst as an example.

Five polymerizations with 0.15 mol% $Ni(IPr)(acac)_2$ were carried out in parallel, and terminated at 0.5, 1.0, 1.5, 10, 30 min. Workup process was identical to the general procedure as described above. Detailed data are shown in Table S3.

Synthesis of block polymer:

The solution of 2-bromo-5-magnesiumchloride-3-ethylhexylthiophene (**2**) (0.10 mol/L) with 1,4-dioctyloxybenzene as internal reference was prepared in a procedure identical to that of **1**. $Ni(IPr)(acac)_2$ (5 mmol/L in THF, 0.25 mL, 1.25 μmol) was added to a solution of **2** (2.5 mL, 0.25 mmol) in 10 mL flask for polymerization. After 2 min, monomer **1** (2.5 mL, 0.25 mmol) was added and the polymerization was continued for 8 min. The polymerization was terminated with 2 mL aqueous HCl (5 mol/L), and then $CHCl_3$ (70 mL) was added for dissolving the polymer. The organic phase was washed with water and dried with $MgSO_4$. The solvent was removed, and the polymer was precipitated in methanol from $CHCl_3$ solution. The crude polymer were collected and then purified by Soxhlet extraction with methanol and then hexane to afford P3EHT-*b*-P3HT. Yield: 85% (74 mg). M_n = 176 kg/mol, PDI = 1.19. ^{1}H NMR ($CDCl_3$, 50 °C): δ (ppm) 6.99 (s, 1H), 6.96 (s, 0.72H), 2.82 (t, 2H), 2.76 (d, 1.48H), 1.72-0.92 (m, 24H).

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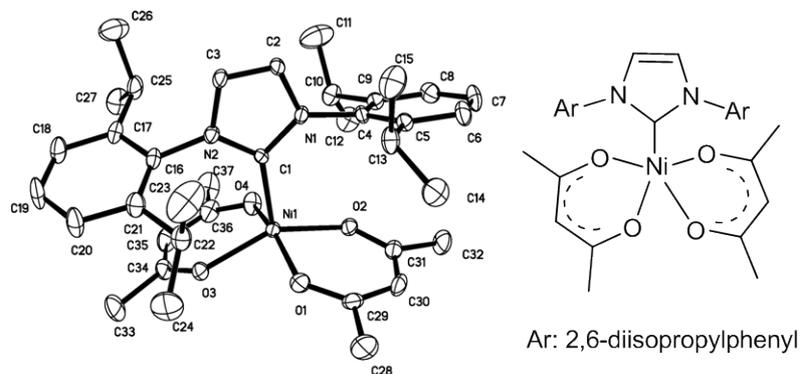
Figure S1. Chemical and crystal structures of Ni(IPr)(acac)$_2$. Thermal ellipsoids are drawn at the 30% probability level, and H atoms are omitted for clarity.

Table S1. Bond lengths [Å] and angles [deg] for the complex of Ni(IPr)(acac)$_2$.

Bond length	Å	angle	deg
Ni1-O1	1.981(5)	O1-Ni1-C1	100.7(2)
Ni1-O2	2.007(3)	O2-Ni1-C1	106.5(14)
Ni1-O3	2.009(3)	O3-Ni1-C1	106.18(14)
Ni1-O4	2.000(5)	O4-Ni1-C1	99.3(2)
Ni1-C1	2.042(4)	O1-Ni1-O4	160.00 (15)
		O1-Ni1-O2	88.99(15)
		O4-Ni-O4	85.09(15)
		O1-Ni1-O3	85.64(15)
		O4-Ni1-O3	89.07(15)
		O2-Ni-O3	147.31 (14)

Table S2 Crystallographic data for the complex Ni(IPr)(acac)$_2$.

	Ni(IPr)(acac)$_2$
Empirical formula	C$_{37}$H$_{50}$N$_2$NiO$_4$
Formula weight	645.50
Crystal system	orthorhombic
Space group	Pca2$_1$
a (Å)	15.7155 (8)
b (Å)	20.8328 (10)
c (Å)	21.8429 (11)
α (deg)	90
β (deg)	90
γ (deg)	90
Volume (Å^3), Z	7151.3(6), 8
Density (Mg/m^3)	1.199
Absorp coeff (mm^{-1})	0.581
F(000)	2768
Limiting indices	-18 <=h <=18,
	-24 <= k <=24,
	-25<=1<= 25
ɵ range for data collection (deg)	1.62 to 25.06
Reflections collected	12365
Independent reflections	9620 (R$_{int}$ =0.0671)
Absorption correction	Semi-empirical from equivalents
Data / restraints / parameters	12365/16/793
Goodness-of-fit on F^2	1.061
Final R indices [I>2σ (I)]：R$_1$,wR2	0.0671,0.1741
R indices (all data)	0.0858,0.1924

Table S3. Polymerization results of **1** with 0.15 mol % of Ni(IPr)(acac)$_2$ at different time.[a]

Entry	Time (min)	M_n[b] (kg/mol)	PDI[b]	TOF[d] (min^{-1})	Conv[c] (%)
1	0.5	36.0	1.13	240	18.4
2	1	75.0	1.19	196	30.2
3	1.5	83.0	1.33	177	40.9
4	10	224	1.36	62	94.8
5	30	228	1.33	21	95.1

[a]All polymerizations were carried out at 25 °C in the presence of 1 equiv LiCl with $[1]_0 = 0.10$ mol/L. [b] Measured by GPC at 150 °C in 1,2,4-C$_6$Cl$_3$H$_3$ with polystyrene as standard. [c]Measured by GC. [d] Turnover frequency (TOF).
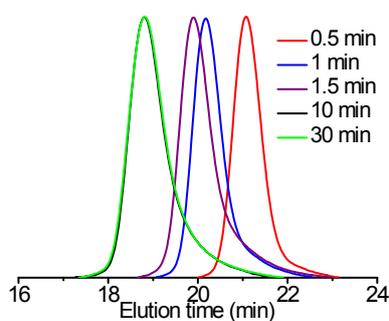
Figure S2. GPC elution curves of P3HTs prepared form the polymerizations with 0.15 mol % Ni(IPr)(acac)$_2$ and different termination times.
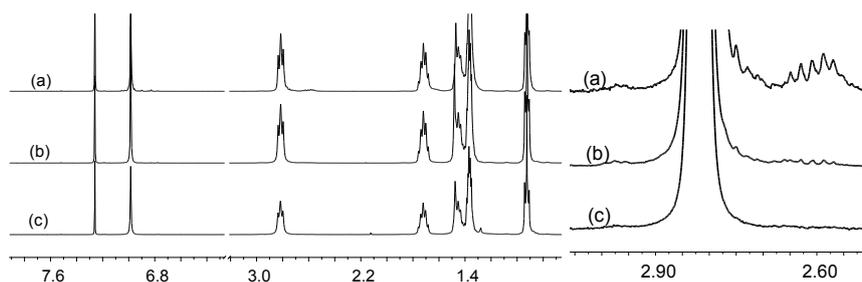
Figure S3. ^{1}H NMR spectrum of P3HT with different molecular weight (a) M_n =19.9 kDa, PDI = 1.23; (b) M_n = 98.0 kDa, PDI = 1.21; (c) M_n = 262 kDa, PDI = 1.21.

Scheme S1. Synthesis of Block Copolymer P3EHT-*b*-P3HT with 0.50 mol% Ni(IPr)(acac)₂ as the Catalyst.

R = *n*- hexyl, R₁= 2-ethylhexyl
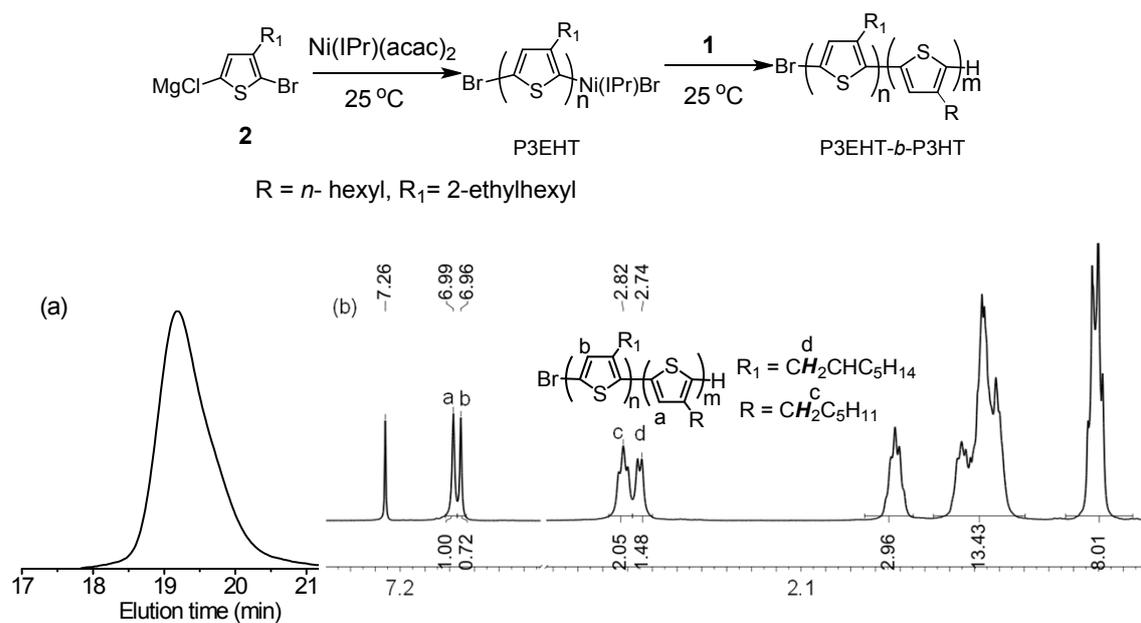
Figure S5. GPC elution curves (a) and ^{1}H NMR of spectrum (400 MHz, CDCl₃, 50 °C) (b) of P3EHT-*b*-P3HT (M_n = 176 kg/mol, PDI = 1.19).

IPrNi-a   IPrNi-b   HT-HT-Ni(IPr)Br

dpppNi-a   dpppNi-b   HT-HT-Ni(dppp)Br

C
N
Ni
S
Br
P
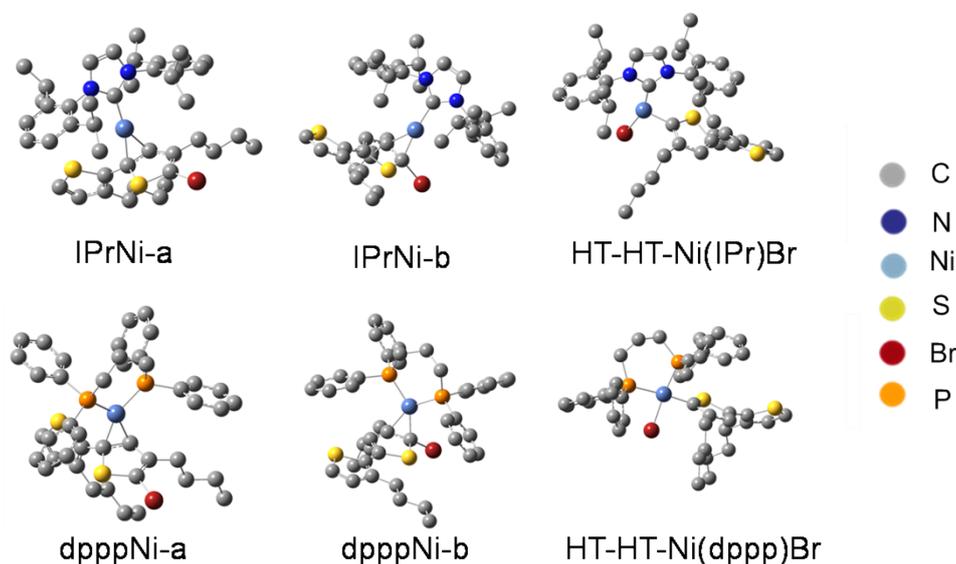
Figure S5. Optimized structures of Ni-complexes using DFT calculations.
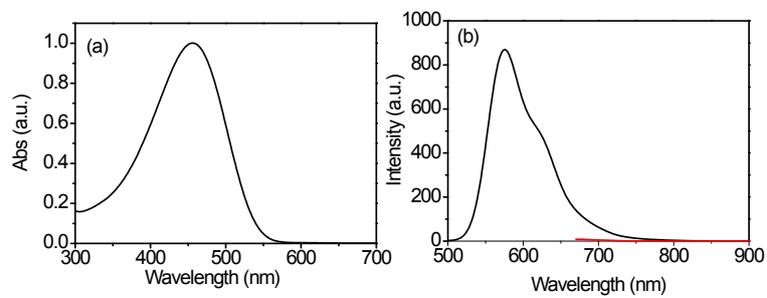
Figure S6. UV-vis absorption (a) and fluorescence (b) spectra of P3HT (M_n = 98.0 kg/mol, PDI = 1.21) in $CHCl_3$ (2×10^{-4} mol/L of repeating unit).