A Ni^{0}(cod)(dq) (COD: 1,5-cyclooctadiene; DQ: duroquinone) complex as a catalyst precursor for oligothiophene and polythiophene synthesis

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Ni^0(cod)(dq) (COD: 1,5-cycloctadiene; DQ: duroquinone) complex as a catalyst precursor for oligothiophene and polythiophene synthesis

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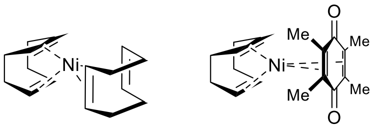
Nickel-catalyzed syntheses of oligothiophene and polythiophene were carried out with Ni(cod)(dq) (COD: 1,5-cycloctadiene; DQ: duroquinone) as a catalyst precursor. Studies on ligand exchange of Ni(cod)(dq) revealed that a high temperature was necessary to replace COD and DQ with PPh_3 and N-heterocyclic carbene IPr. A coupling reaction of a metalated 3-hexylthiophene with 2-chloro-3-hexylthiophene employing Ni(cod)(dq) with IPr proceeded with a remarkably reduced amount of homocoupling byproduct. Polymerization of 2-chloro-3-hexylthiophene with Ni(cod)(dq)/DPPP also resulted to reduce the regioregularity defect.

Introduction

Extensive studies have been devoted to the development of transition metal-catalyzed coupling reactions in organic synthesis.[1,2] Among those, nickel and palladium have played a key role in the field of cross coupling. The reaction allows formation of a wide range of carbon–carbon and carbon–heteroatom bonds highly efficiently. Compared to the use of palladium as a catalyst, which is relatively tolerant of oxygen contamination, zero-valent nickel is more sensitive to oxygen and often requires a rigorous Schlenk technique or handling in a glove box to carry out the catalytic reaction efficiently.[3] $Ni(cod)_2$ (COD: 1,5-cycloctadiene) (**1**) has been recognized as a powerful tool as a catalyst precursor of Ni^0 complex, and extensive studies have been carried out with such a catalyst system.[4–12] However, $Ni(cod)_2$ is still sensitive to air and thermally unstable.[13] Therefore, a number of reports on catalytic reactions that use $Ni(cod)_2$ as a catalyst precursor require a large amount of catalyst loading, in general, 5–10 mol% or more suggesting that the reaction is based on the sacrifice of a considerable amount of partial deactivation of thus formed nickel(0) catalyst. Accordingly, in situ formation of a nickel(0) catalyst with nickel(II) along with an appropriate reducing agent has also been an alternative tool to perform the nickel-catalyzed coupling reaction.[14] However, a major drawback of the use of nickel(II) catalyst is the undesired homocoupling as a side reaction, which occurs based on the amount of the catalyst loading. Such a side reaction is particularly problematic in the coupling reaction between a substrate and a reactant with similar polarity as exemplified by a coupling of nonpolar thiophene and thiophene to form a thiophene–thiophene bond because the formation of the side product makes chromatographic separation and purification extremely difficult.[15–17]

Recently, Engle and co-workers reported that Ni(cod)(dq) (DQ: duroquinone) (**2**) was available as a catalyst precursor for several nickel(0)-catalyzed synthetic reactions as a surrogate of $Ni(cod)_2$ because of much improved stability to oxidation and thermal decomposition. [12,18,19] It was also shown that the employment of Ni(cod)(dq) (**2**) along with an appropriate ligand showed comparable reactivities to $Ni(cod)_2$ (**1**) in several coupling reactions such as Suzuki-Miyaura coupling, Buchwald-Hartwig amination, etc. However, despite the remarkable breakthroughs in nickel catalysis, there are surprisingly few reports of subsequent utilization in catalytic synthetic reactions.[20–23]



$Ni(cod)_2$ (**1**) Ni(cod)(dq) (**2**)

Chart 1. $Ni(cod)_2$ (1) and Ni(cod)(dq) (2)

Since much efforts have been paid in the development of practical synthesis of thiophene oligomers and polymers, where nickel complexes bearing a bidentate phosphine ligand or an N-heterocyclic carbene (NHC) ligand has been shown to be highly effective.[24–29] We have also shown that the deprotonative formation of thiophene–metallic species followed by nickel-catalyzed coupling efficiently furnishes

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oligothiophenes and polythiophenes in a practical manner.[30–36] We thus considered that it is intriguing to apply Ni(cod)(dq) complex for the synthesis of thiophene oligomers and polymers. Herein, we report the use of Engle's Ni(cod)(dq) complex (**2**) as a catalyst precursor for the coupling reaction forming thiophene–thiophene bond. The employment of the catalyst precursor **2** revealed that the formation through the undesired homocoupling was remarkably suppressed.

Results and discussion

Since there has been few reports on the ligand exchange of Ni(cod)(dq) (**2**), we first studied the reaction of **2** with triphenyl phosphine that is a ubiquitous ligand in catalysis. The progress of the ligand exchange was monitored by the measurement of ^{31}P NMR analysis. When the reaction was carried out using Ni(cod)(dq) (**2**) and 5 molar amounts of PPh$_3$ in toluene at room temperature, ^{31}P NMR suggested little exchange after the reaction period of 2 h to observe the signal assigned as PPh$_3$ (–5 ppm).[37] Performing the reaction at an an elevated temperature (80 °C) was found to be necessary to undergo the ligand exchange. The measurement of ^{31}P NMR analysis showed that a signal at 26 ppm, which was assigned as PPh$_3$ on nickel(0) (42%),[38] accompanied by remaining 58% of triphenylphosphine after the reaction period of 2 h. The ligand exchange was also monitored by the liberated amount of COD and DQ from **2** by the measurement of GC-MS. As shown in Figure 1(a), addition of PPh$_3$ resulted in the dissociation of almost quantitative amount of COD and DQ from the nickel complex **2** after stirring for >120 min. On the other hand, the removal of COD and DQ hardly occurred at room temperature even after 240 min. We also studied the related ligand exchange with NHC ligand IPr (1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene)[39] in THF. The result was summarized in Figure 1(b). A sluggish ligand exchange of **2** with IPr was shown to occur at room temperature, while the reaction at 60 °C proceeded much faster. Almost quantitative liberation of COD and DQ was observed after stirring for 4 h. The result markedly contrasts with the rapid exchange of Ni(cod)$_2$ (**1**), which has been reported to occur at room temperature within 20 min.[40] Subsequently, these studies shows that the ligand exchange of Ni(cod)(dq) requires harsh conditions compared with the related Ni(cod)$_2$, for which the exchange, in general, occurs even at room temperature.

With the optimum conditions concerning ligand exchange of Ni(cod)(dq) in hand, we examined the cross coupling of metalated thiophene **3'** with chlorothiophene **4a** leading to head-to-tail-type (HT) thiophene dimer **5**.[32] The nickel catalyst species was in situ generated by the reaction of **2** and IPr at 60 °C for 4 h and thus generated catalyst solution was introduced into the reaction of **3'**, which was formed by the reaction of TMPMgCl·LiCl (TMP: 2,2,6,6-tetramethylpiperidin-1-yl)[41] and 2-chloro-3-hexylthiophene (**4a**). When 5 mol% of the nickel(0) catalyst was employed, HT-bithiophene was obtained in 95% yield accompanied by the formation of homocoupling byproduct **6** in only 1.2% yield (Table1, Entry4).

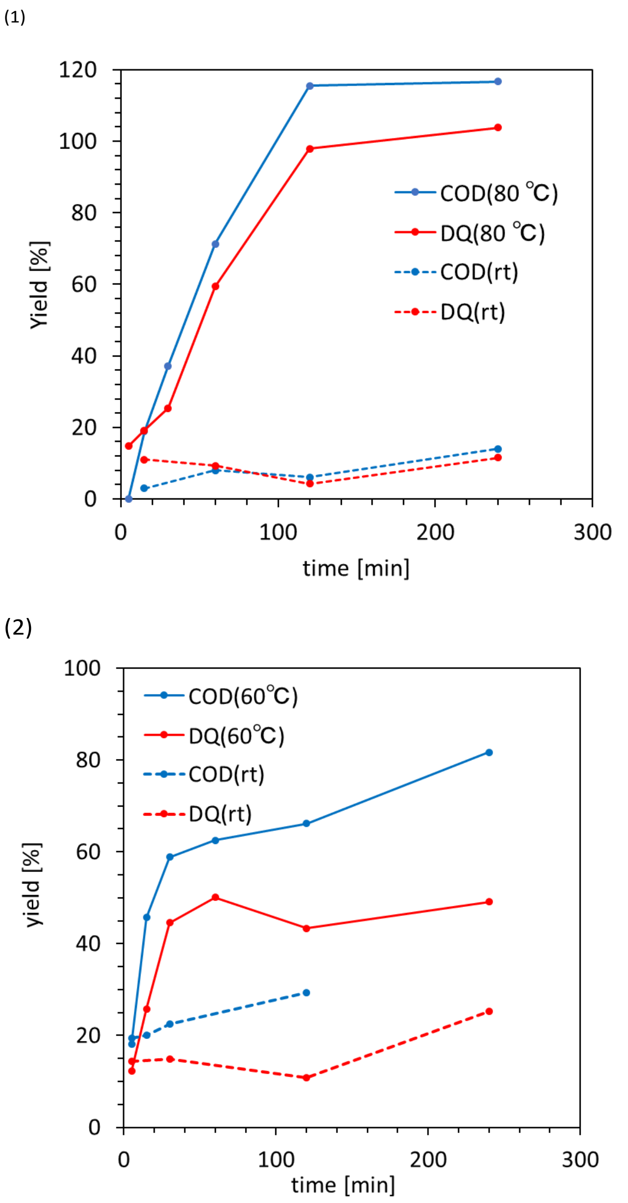
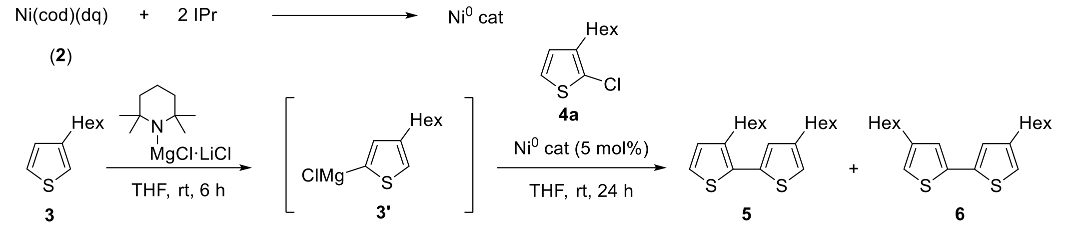


Figure 1. Ligand exchange of Ni(cod)(dq) (2) with (a) PPh$_3$ (in toluene) and (b) N-heterocyclic carbene (NHC) IPr (in THF) analyzed by GC-MS

Further detailed studies were also performed in the reaction of metalated thiophene **3'** and chlorothiophene **4a**. As shown in Table 1, indeed, the reaction of **3** and **4a** in the presence of 5 mol% of nickel(II) catalyst NiCl$_2$(IPr)PPh$_3$[42] furnished 4% of undesired homocoupling byproduct **6**, which was consistent with the amount of catalyst loading, accompanied by 88% of **5** as desired head-to-tail bithiophene. We next carried out the reaction with freshly purchased Ni(cod)$_2$ (**1**) and IPr as a ligand under similar conditions. The reaction with 5 mol% of the nickel catalyst resulted the formation 3.6% of byproduct accompanied by 74% of desired HT bithiophene **5**, suggesting that Ni(cod)$_2$ (**1**) was unintendedly oxidized even under Schlenk conditions and thus formed nickel(II) species allowed to furnish homocoupling byproduct. These results contrast with the reaction of Ni(cod)(dq) (**2**)/IPr that formed homocoupling byproduct **6** in

Table 1. The reaction of 3-hexylthiophene (3) with 2-chloro-3-hexylthiophene (4a) leading to head-to-tail (HT) bithiophene dimer 5[a]



Entry	Nickel	mol%	Ligand NHC (mol%)[b]	Yield[c] 5	 6
1	NiCl$_2$(PPh$_3$)IPr	5	–	88%	4.0%
2	Ni(cod)$_2$ (**1**)	5	IPr (10)	74%	3.6%
3	**1**[d]	5	IPr (10)	0%	0%
4	Ni(cod)(dq) (**2**)	5	IPr (10)	95%	1.2%
6	**2**	2	IPr (4)	64%	0.5%
7	**2**	10	IPr (20)	87%	2.6%
8	**2**	5	–[e]	0%	2.3%
9	**2**	5	SIPr[f] (10)	80%	1.3%
10	**2**	5	IMes[g] (10)	24%	2.3%
11	**2**	5	SIMes[h] (10)	31%	1.3%

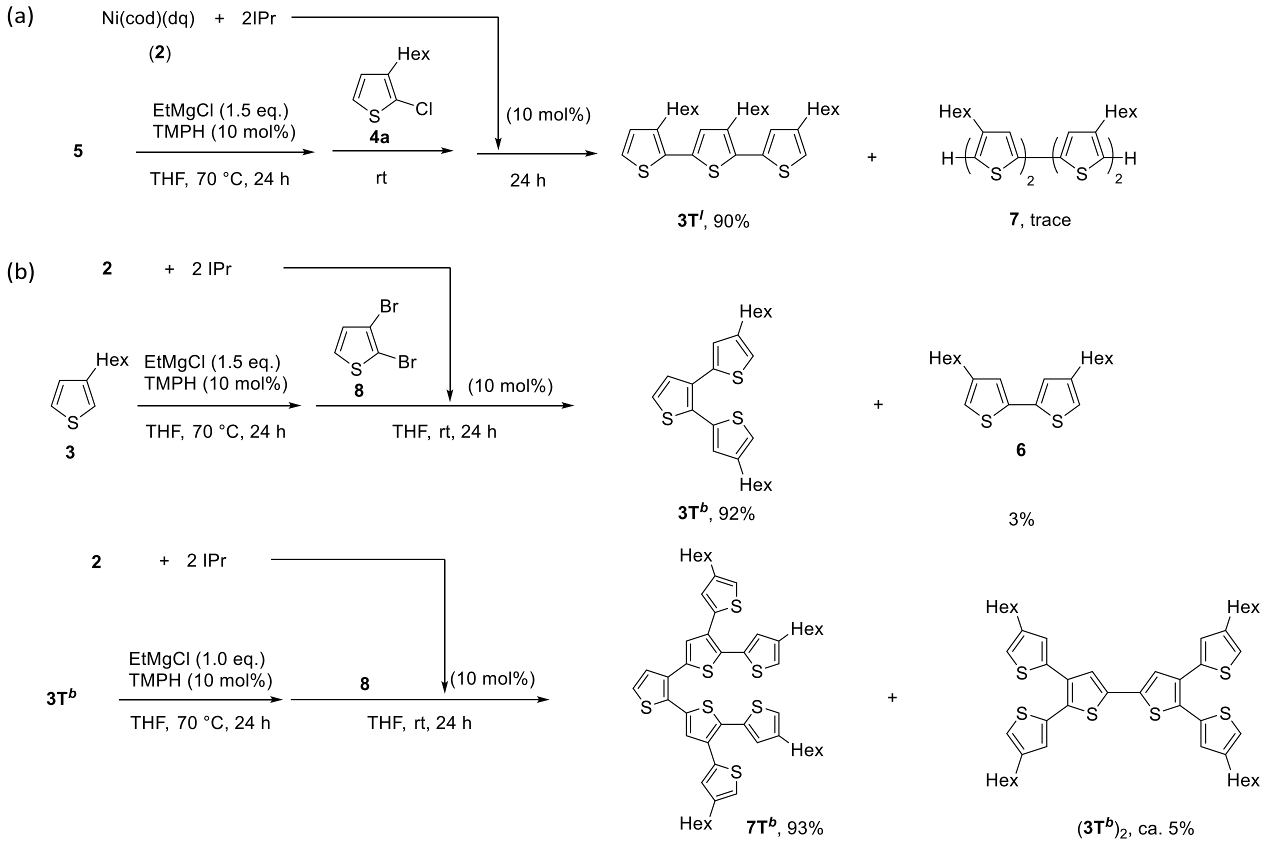
[a] The reaction was performed with **3** (0.6 mmol) and **4a** (0.5 mmol) in 1.0 mL of THF. [b] The ligand was in situ generated form the corresponding HCl salt with NaO^{t}Bu as a base in THF and addition of catalyst **2** followed to form the nickel complex. [c] The yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard. [d] After storage for 3 weeks in the freezer. [e] Absence of NHC ligand. [f] 1,3-Bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene [g] 1,3-Dimesitylimidazol-2-ylidene [h] 1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene

only 1.2%. It should also be pointed out that no reaction took place when the nickel catalyst **1** was used after the storage in the freezer under inert conditions for 3 weeks. The reaction with further reduced catalyst loading (2 mol%) decreased the formation of homocoupling to give **6** to 0.5%, while the increase of the catalyst loading to 10 mol% resulted in only 2.6% of homocoupling **6**. The attempted reaction in the absence of NHC ligand afforded little HT bithiophene **5** and only 2.3% of homocoupled **6** as shown in entry 8.

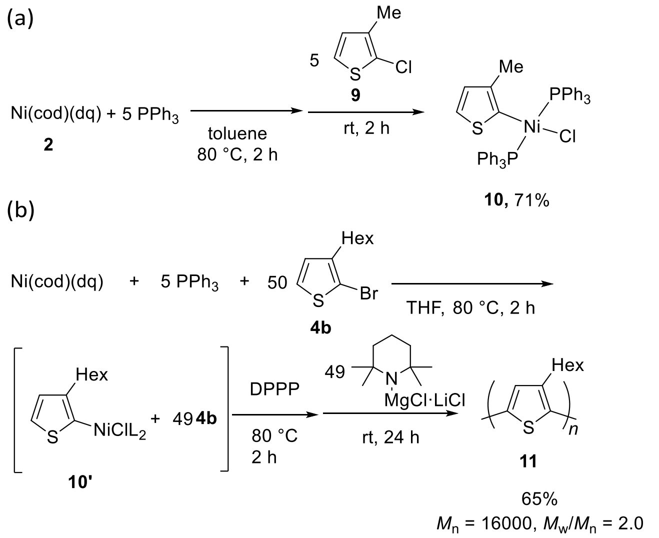
The reaction also proceeded similarly with SIPr (entry 9). However, other NHC ligands (IMes and SIMes)[43] significantly decreased the yield. (entry 10 and 11) Although the formation of undesired homocoupling **6** was not completely suppressed, the yield of **6** was remarkably decreased irrespective of the amount of catalyst loading (2–10 mol%).

We next envisaged to synthesize further linear and branched thiophene oligomers.[15,32] When the obtained bithiophene **5** was subjected to the reaction of a Grignard reagent in the presence of 10 mol% of TMPH[31,44] to undergo metalation and following treatment with chlorothiophene **4a** using 10 mol% of Ni(cod)(dq) (**2**) /2IPr in a similar manner, the corresponding linear terthiophene **3T**^{l} was obtained in 90% yield accompanied by a trace amount of homocoupling byproduct tetramer **7**.

The synthesis of the branched oligothiophenes were also achieved successfully in a similar manner using nickel complex **2** and IPr as shown in Scheme 1b. The cross-coupling reaction of metalated thiophene generated by EtMgCl/TMPH was treated with 2,3-dibromothiophene (**8**) in the presence of 10 mol% of Ni(cod)(dq)/2IPr at room temperature. The branched oligothiophene **3T**^{b} was obtained in 92% yield after stirring for 24 h, while the amount of homocoupling byproducct **6** was much smaller than the catalyst loading. The branched oligomer **3T**^{b} was also metalated by EtMgCl/TMPH and cross-coupling reaction with dibromothiophene **9** using 10 mol% of Ni(cod)(dq)/2IPr followed. After stirring at room temperature for 24 h, the corresponding further oligomer composed of seven thiophene units **7T**^{b} was produced in 93% yield (homocoupling byproduct <5%).



Scheme 1. (a) Stepwise synthesis of linear thiophene oligomer, (b) Synthesis of branched thiophene oligomer



Scheme 2. Polythiophene synthesis with Ni(cod)(dq) (2) as a catalyst precursor: (a) by external initiator 10 and (b) one-pot protocol

Unlike the synthesis of thiophene oligomers by cross-coupling, where the use of nickel (II) leads to the formation of the homocoupling byproduct, the side reaction is reflected to the incorporation into the polymer backbone as a regioregularity defect in polythiophene synthesis.[26,45] Thus, it becomes a particularly serious problem in obtaining low degree of polymerization polythiophenes using large amounts of catalyst. We first examined the formation of tihophene–nickel complex **10** with Ni(cod)(dq) (**2**). Addition of 2-chloro-3-methylthophene **9** to the reaction mixture of **2** and PPh_3 induced oxidative addition to afford **10** in 71% yield after stirring at room temperature for 2 h (Scheme 2a).[46] Encouraged by the smooth formation of thiophene–nickel(II) complex **10** by oxidative addition, one-pot formation of nickel(II) complex/cross-coupling polymerization of 2-bromo-3-hexylthiophene (**4b**) was examined.[47] As shown in Scheme 2b, Ni(cod)(dq) (**2**) was treated with PPh_3 and **4b** to form nickel(II) complex **10'**, in which 49 fold **4b** would remain. Sequential addition of bidentate phosphine DPPP (80 °C, 2 h) and 49 fold excess TMPMgCl·LiCl) (dropwise addition at room temperature) underwent ligand exchange and deprotonation to afford the corresponding polythiophene **11** in 65% yield (M_n= 16000, M_w/M_n = 2.0) after stirring at room temperature for 24 h. When 10-fold excess of thiophene **4b** was employed toward nickel catalyst, polythiopehene **11** was obtained in 33% yield. Figure 2 compares the regioregularity of polymer **11** with (a) nickel(II) vs. (b) nickel(0) by ^{1}H NMR analysis. In the average degree of polymerization ca. 10–11 the regioregularity defect was observed at ca. 2.68–2.75 ppm in the use of nickel(II) catalyst, while one-pot protocol with Ni(cod)(dq) as a catalyst precursor remarkably decreased the defect.[48]

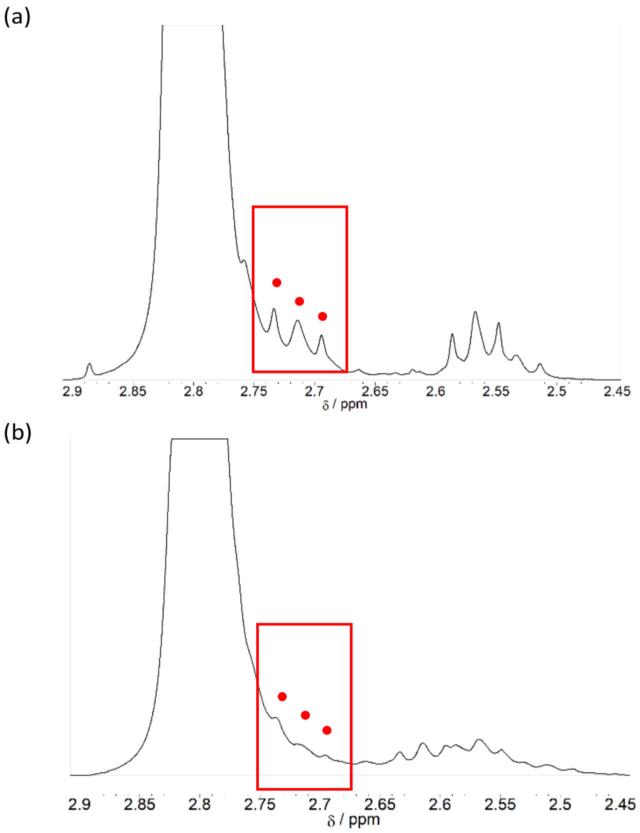


Figure 2. Comparison of regioregularity defect in polythiophene synthesis with 10 mol% (a) $Ni^{II}Cl_2$(dppp) and (b) Ni(cod)(dq) (2) as a catalyst precursor

Conclusions

In conclusion, we have shown that the use of Ni(cod)(dq) as a benchtop catalyst precursor for nickel-catalyzed cross-coupling of oligothiophenes and polythiophene. Oligothiophenes and polythiophene were synthesized in excellent yields with reduced formation of undesired homocoupling side product that is afforded in the use of nickel(II), instead of nickel(0), based on employed amount of the catalyst. With these methods, a wide variety of well-defined linear and branched oligothiophene derivatives can be synthesized in a standard Schlenk technique without the use of the glove box.

Data availability

Experimental details, copies of NMR spectra, and the related references can be found in ESI.

Author Contributions

A. M. conceived the ideas and designed the project. N. N. performed coupling reactions of thiophenes, S. Y. engaged in the studies on ligand exchange, U. O. performed polythiophene synthesis, M. H. and K. O. performed spectroscopic analyses and suggestions on synthetic protocols. A. M. wrote the manuscript with contributions from all authors.

Conflicts of interest

There are no conflicts to declare.

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‡ The authors cicted additional references within the Supporting Information.[49,50]

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