

# Influence of Alkyl Substitution Pattern on Reactivity of Thiophene-Based Monomers in Kumada Catalyst-Transfer Polycondensation

*Roman Tkachov, Volodymyr Senkovskyy,\* Hartmut Komber, and Anton Kiriya\**

Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany

AUTHOR EMAIL ADDRESS [senkovskyy@ipfdd.de](mailto:senkovskyy@ipfdd.de); [kiriya@ipfdd.de](mailto:kiriya@ipfdd.de)

## **Experimental Part.**

### **Instrumentation.**

$^1\text{H}$  (500.13 MHz) and  $^{31}\text{P}$  (202.46 MHz) *NMR spectra* were recorded on a Bruker Avance III spectrometer using a 5 mm  $^1\text{H}/^{13}\text{C}/^{19}\text{F}/^{31}\text{P}$  gradient probe. The  $^1\text{H}$  spectra of P3HT were recorded at 303 K using  $\text{CDCl}_3$  as solvent and were referenced on the residual solvent peak (7.26 ppm). The  $^{31}\text{P}$  NMR spectra were recorded using  $\text{THF-d}_8$  as solvent and referenced on external  $\text{H}_3\text{PO}_4$  ( $\delta = 0$  ppm).

The samples for in-situ NMR experiments were prepared under argon atmosphere. For that,

For in-situ NMR investigations, Grignard monomers (**1-4**) were prepared in a usual way, solvent (THF) was evaporated under vacuum to the dryness and remaining solid was dissolved in dry  $\text{THF-d}_8$  under argon. A respective amount of  $\text{Ni(dppe)Cl}_2$  (or  $\text{Ni(dppe)Cl}_2$ ) was placed into NMR tube which was then closed with a septum, cooled down to  $-20\text{ }^\circ\text{C}$  and an aliquot of the  $\text{THF-d}_8$  monomer solution was added with a syringe.

*GPC measurements* were carried out on Agilent 1100 Series (Agilent, USA) normal-temperature size exclusion chromatograph, equipped with refractive index detector and one column PL Gel MIXED-B (Polymer Laboratories, UK), eluent – chloroform and flow rate 1 mL/min. Number average molecular weights ( $M_n$ ) and polydispersity indexes (PDI) of obtained polymers were determined based on calibration with polystyrene standards obtained from Polymer Standards Service (PSS, Germany).

**Materials.** 2-Bromo-3-hexyl-5-iodothiophene,<sup>1</sup> diethyldipyridylnickel (NiEt<sub>2</sub>bpy),<sup>2</sup> and Ph-Ni(dppp)-Br and Ph-Ni(dppe)-Br [ref 16 of the main text] were synthesized as described elsewhere. Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl. All other chemicals were purchased from Aldrich and used as received.

### **Synthesis of 5-bromo-3-hexyl-2-iodothiophene and the monomer 1.**

5-bromo-3-hexyl-2-iodothiophene was synthesized by sequential iodination and bromination of 3-hexylthiophene as described below. N-iodosuccinimide (NIS) (4.73 g, 0.021 mol) was added to the solution of 3-hexylthiophene (3.37 g, 0.02 mol) in 50 mL chloroform-acetic acid mixture (50/50 v/v) in the absence of light, under an argon atmosphere, at temperature 0°C. The mixture was allowed to reach room temperature and stirred overnight. Then, the mixture was poured into 200 mL of ice-water, organic layer was separated and the aqueous phase extracted with chloroform. The combined extracts were washed with water, 1 M sodium hydroxide solution (50 ml), again with water, dried (MgSO<sub>4</sub>), and concentrated. The residue was purified by flash chromatography to give 5.2 g of 3-hexyl-2-iodothiophene (90% yield). Bromination was performed in a similar manner. To this end, N-bromosuccinimide NBS (3.382 g, 19 mmol) was added to 3-hexyl-2-iodothiophene (5.2 g, 17.68 mmol) in 50 mL of a chloroform-acetic acid mixture (50/50 v/v) in the absence of light, under an argon atmosphere, at temperature 0°C. The mixture was allowed to reach room temperature, stirred overnight, and then worked up according to above-described procedure. Purification by flash chromatography yielded 3.63 g (55%) of 5-bromo-3-hexyl-2-iodothiophene (Figure S1).

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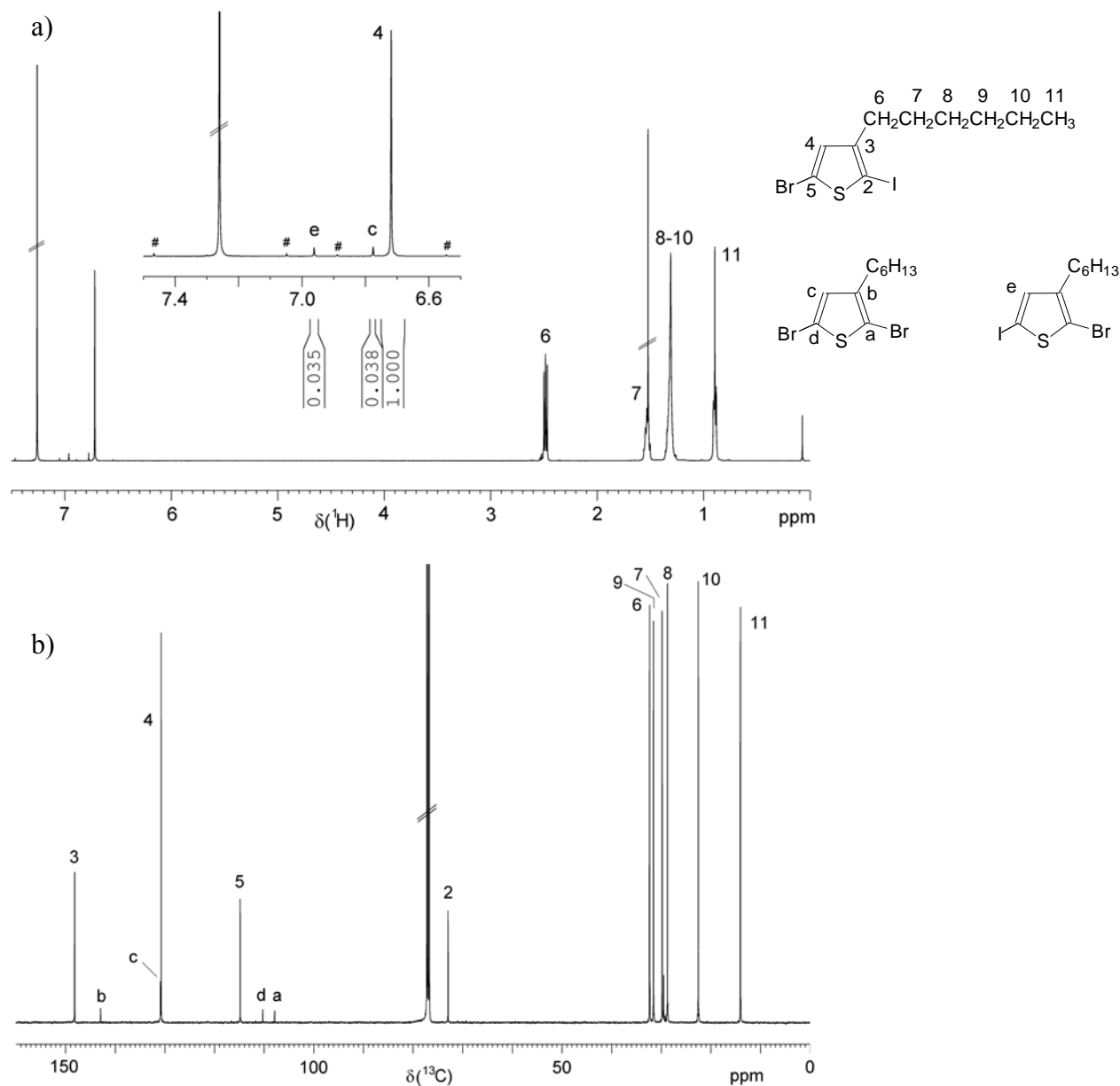
<sup>1</sup> Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169. Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542.

<sup>2</sup> Wilke, G.; Herrmann, G. *Angew. Chem. Int. Ed.* **1966**, *5*, 581-582.

### NMR data of 5-bromo-3-hexyl-2-iodothiophene

$^1\text{H}$  NMR: 6.72 (H<sub>4</sub>), 2.49 (H<sub>6</sub>), 1.54 (H<sub>7</sub>), 1.4 – 1.25 (H<sub>8</sub>-H<sub>10</sub>), 0.90 (H<sub>11</sub>).

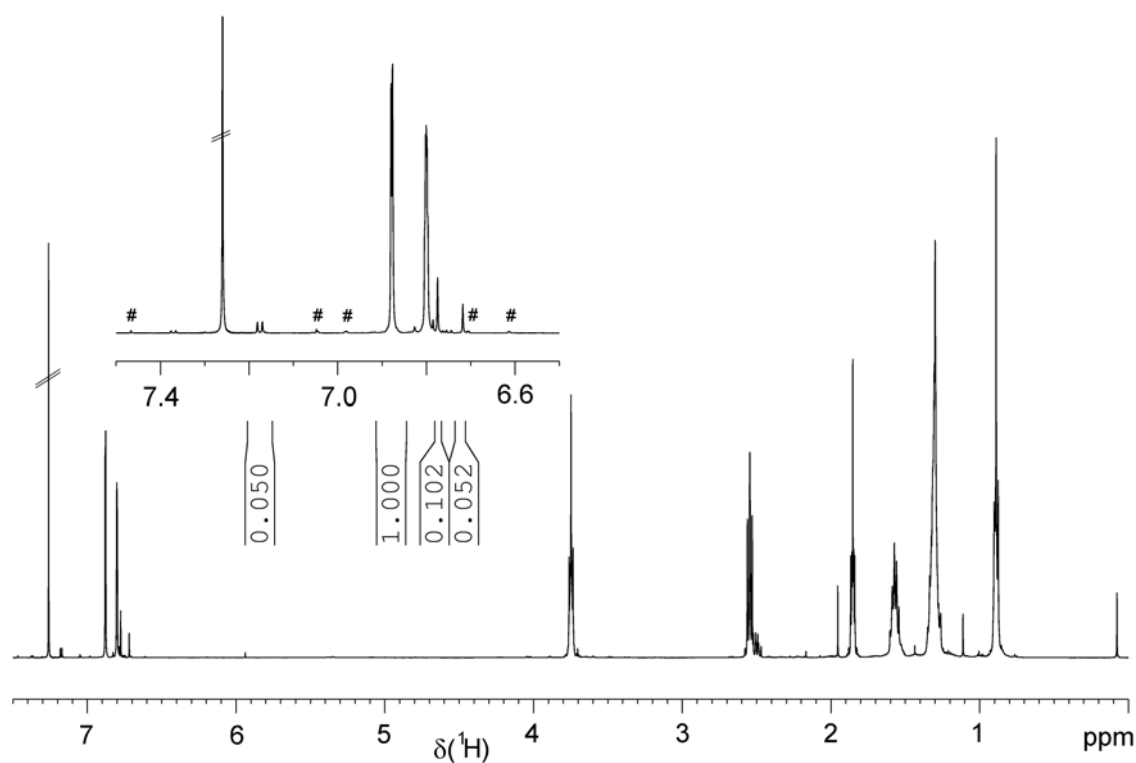
$^{13}\text{C}$  NMR: 148.20 (C<sub>3</sub>), 130.77 (C<sub>4</sub>), 114.84 (C<sub>5</sub>), 72.97 (C<sub>2</sub>), 32.35 (C<sub>6</sub>), 31.58 (C<sub>9</sub>), 29.83 (C<sub>7</sub>), 28.77 (C<sub>8</sub>), 22.55 (C<sub>10</sub>), 14.06 (C<sub>11</sub>).



**Figure S1.** (a)  $^1\text{H}$  NMR spectrum of the 5-bromo-3-hexyl-2-iodothiophene showing about 3.5% impurity of 2-bromo-3-hexyl-5-iodothiophene and 2,5-dibromo-3-hexyl-thiophene. Signals marked with # are  $^{13}\text{C}$  satellites. (b)  $^{13}\text{C}$  NMR spectrum of 5-bromo-3-hexyl-2-iodothiophene containing about 8% 2,5-dibromo-3-hexyl-thiophene (solvent:  $\text{CDCl}_3$ ).

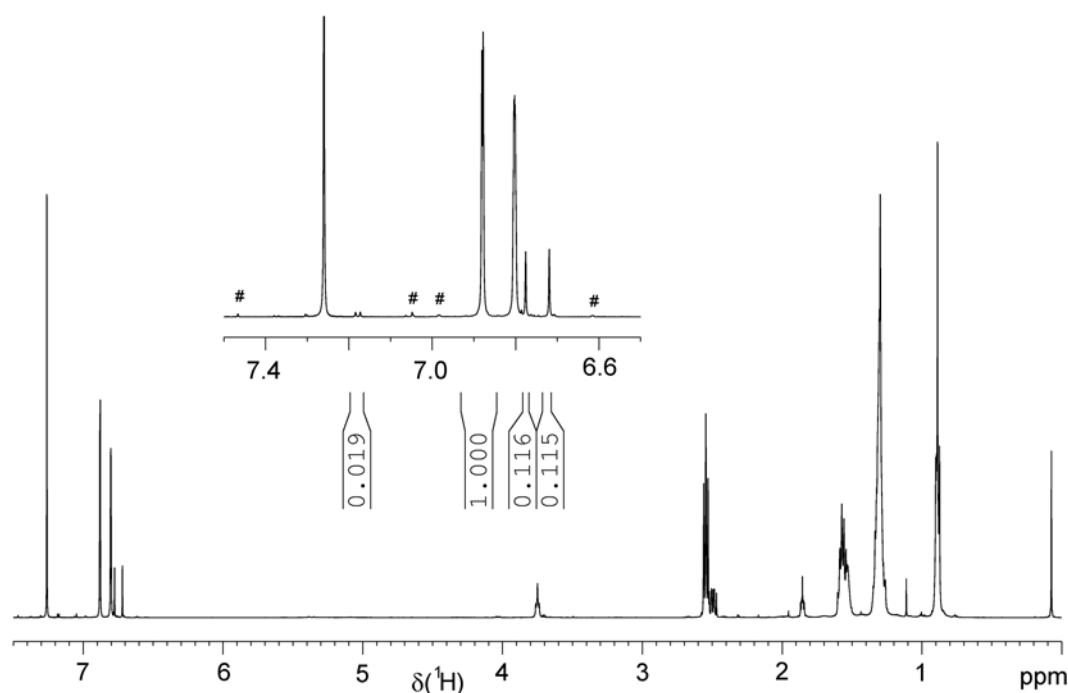
Conversion of the precursor into the monomer was performed as follows.

**Method 1)** To the solution of 5-bromo-3-hexyl-2-iodothiophene (0.373g, 1mmol) in 10 ml of dry THF, 1ml of t-BuMgCl solution in THF (1M) was added under argon at 0°C. The mixture was stirred for 1 h at 0°C before used in further experiments. This procedure leads to the mixture of monomers **1** and **2** in a 95/5 proportion (Figure S2).



**Figure S2:** <sup>1</sup>H NMR spectrum of the monomer 1 prepared at 0°C and further quenched with water which shows about 5% of impurity of the monomer 2. Signals marked with # are <sup>13</sup>C satellites.

**Method 2)** To the solution of 5-bromo-3-hexyl-2-iodothiophene (0.373g, 1mmol) in 10 ml of dry THF, 0.94 ml of t-BuMgCl solution in THF (1M) was added under argon at -30°C. The mixture was allowed to warm to -10°C within 1 hour and further to 0°C within the next 1 hour before used in further experiments. This procedure allowed to reduce the content of the monomer 2 in the mixture below 2% (Figure S3).



**Figure S3:**  $^1\text{H}$  NMR spectrum of the monomer **1** prepared at  $-30^\circ\text{C}$  to  $-10^\circ\text{C}$   $0^\circ\text{C}$  and further quenched with water with the content of the monomer **2** below 2% and about 10% of unreacted monomer precursors. Signals marked with # are  $^{13}\text{C}$  satellites.

### Synthesis of 2-bromo-3,4-dihexyl-5-iodothiophene and the monomer **3**.

#### a) Synthesis of 3,4-dihexylthiophene

Magnesium turnings (2.54g, 106 mmol) were placed into a double neck round bottom flask equipped with a reflux condenser, a teflon-coated magnetic stirr bar and a rubber septum. The flask was evacuated and back-filled with dry argon. Dry diethylether (1ml) and 1,2-dibromoethane (0.005ml) were added and the mixture was stirred until evolution of ethylene gas was no longer observed. Then, dry diethyl ether (50 ml) was added, followed by the dropwise addition of 1-bromohexane (17.49g, 106 mmol) during 30 minutes. Finally, the mixture was stirred under reflux for 1 hour. After cooling to room temperature, the Grignard solution was withdrawn via syringe and filtered into an argon filled storage flask. Separately, 2,3-dibromothiophene (9.68g, 40 mmol),  $\text{Ni(dppp)Cl}_2$  (0.217g, 0.4mmol) were placed into a double neck round bottom flask equipped with a reflux condenser, a teflon-coated magnetic stirr bar and a rubber septum. The flask was evacuated and back-filled with dry argon. Dry diethyl ether (50ml) was added followed by the dropwise addition of Grignard solution. Reaction mixture was refluxed overnight, cooled down, quenched by saturated  $\text{NH}_4\text{Cl}$  water solution ( $\sim 10\text{ml}$ ) and poured into water ( $\sim 200\text{ml}$ ). Organic layer was separated, washed with

saturated NaHCO<sub>3</sub> solution, brine, and dried with anhydrous magnesium sulfate. Solvent was removed on rotary evaporator and residue was purified by flash chromatography on SiO<sub>2</sub> eluting with hexane yielding pure 3,4-dihexylthiophene colorless oil ( 8.84 g, 91%. <sup>1</sup>H NMR(500MHz, CDCl<sub>3</sub>) 6.88 (s, 2 H), 2.54 - 2.46 (m, 4 H), 1.66 - 1.57 (m, 4 H), 1.42 - 1.17 (m, 12 H), 0.88 (t, *J* = 6.9 Hz, 6 H)

#### **b) Synthesis of 2-bromo-3,4-dihexylthiophene**

*N*-Bromosuccinimide (0.765g, 4.3mmol) was added in small portions to the solution of 3,4-dihexylthiophene (1.06g, 4.2mmol) in 10ml of 1:1(vol) CHCl<sub>3</sub>-CH<sub>3</sub>COOH mixture at 0°C under argon. Reaction was allowed to proceed overnight, poured into water, extracted with CHCl<sub>3</sub>. Organic layer was sequentially washed with NaHSO<sub>3</sub>, NaHCO<sub>3</sub> solutions, water, dried with MgSO<sub>4</sub> and filtered. Filtrate was evaporated to the dryness, residue was subjected to column chromatography on SiO<sub>2</sub> (hexane) yielding pure 2-bromo-3,4-dihexylthiophene as colorless oil (1.28g, 92%) <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>) δ 6.84 (s, 1 H), 2.54 - 2.46 (m, 4 H), 1.64 - 1.55 (m, 2 H), 1.51 - 1.43 (m, 2 H), 1.41 - 1.18 (m, 12 H), 0.88 (t, *J* = 6.9 Hz, 6 H)

#### **c) Synthesis of 2-bromo-3,4-dihexyl-5-iodothiophene**

Iodination of 2-bromo-3,4-dihexylthiophene was done similarly to bromination.

#### **d) Synthesis of 2-bromo-3,4-dihexyl-5-chloromagnesiiothiophene**

To the solution of 2-bromo-3,4-dihexyl-5-iodothiophene (0.457g, 1mmol) in 10 ml of dry THF, 1ml of *t*-BuMgCl solution in THF (1M) was added under argon at 0°C. The mixture was stirred for 1 h at 0°C before used in further experiments.

**Polymerization experiments.** The monomer **1-4** were prepared as follows: 1 mmol of a respective monomer precursor (i.e., 2-bromo-3-hexyl-5-iodothiophene, or 5-bromo-3-hexyl-2-iodothiophene, or 2-bromo-3,4-dihexyl-5-iodothiophene, or 2-bromo-5-iodothiophene) was placed in a round-bottomed flask equipped with a magnetic stirr bar, the atmosphere was replaced with argon and cooled down to 0°C. THF (6 mL) and tert-butylmagnesium chloride (1M solution, 1 mL, 1 mmol) were added via syringe and the mixture was stirred at 0°C for 1 h. To perform polymerization, the respective initiator Ph-Ni(dppp)-Br (or Ph-Ni(dppe)-Br, or Ph-Ni(dppp)-Br, or Ni(dppp)Cl<sub>2</sub>, or Ni(dppe)Cl<sub>2</sub>) dissolved or suspended in a small quantity of THF was added in one portion to the monomer solution. The mixture was stirred at room temperature and then quenched by a small amount of ~1.25 M HCl/MeOH solution. The

reaction mixture was poured into water and extracted with  $\text{CHCl}_3$ . The combined organic layers were washed with brine, dried over anhydrous  $\text{MgSO}_4$  and concentrated under reduced pressure. Finally, MeOH was added to the residue, the insoluble material was collected by filtration, washed with hot MeOH to give pure P3HT. In cases of low MW products, separation of solids and methanol extracts was done by centrifugation.

### **Polymerization of the monomer 1 contained 3 % of 2 by dppp-supported initiators.**

Although the pure monomer **1** does not polymerize in the presence of  $\text{Ni(dppp)Cl}_2$  even at prolonged (24 hours) stirring at room temperature, “impure” monomer **1** contained 3 % of **2** underwent a slow polymerization at RT when mixed with  $\text{Ni(dppp)Cl}_2$  with 30/1 ratio. Thus, about 18, 27 and 38 % of the monomer **1** was converted into P3HT upon polymerization conducted for 1, 5 and 20 hours, respectively. As it should be for polymerization of reversed monomer **1**,  $^1\text{H}$  NMR spectrum of the resulting P3HT contains characteristic doublet at 7.15 ppm of the terminal hydrogen atom, which is not observed in the spectra of P3HTs formed upon polymerization of the regular monomer **2**. The resulting polymer possessed very high MW reflecting that polymerization was initiated not by all  $\text{Ni(dppp)Cl}_2$  added but only a small part of it. This is consistent with the assumption that the polymerization was initiated by asymmetric initiators **9** or **10** formed via intermediate **7** from **1**, **2** and  $\text{Ni(dppp)Cl}_2$  (Scheme 2 of the main text) similarly to the case of the  $\text{Ni(dppe)Cl}_2$ -catalized polymerization, however the chain-propagation here is very slow.

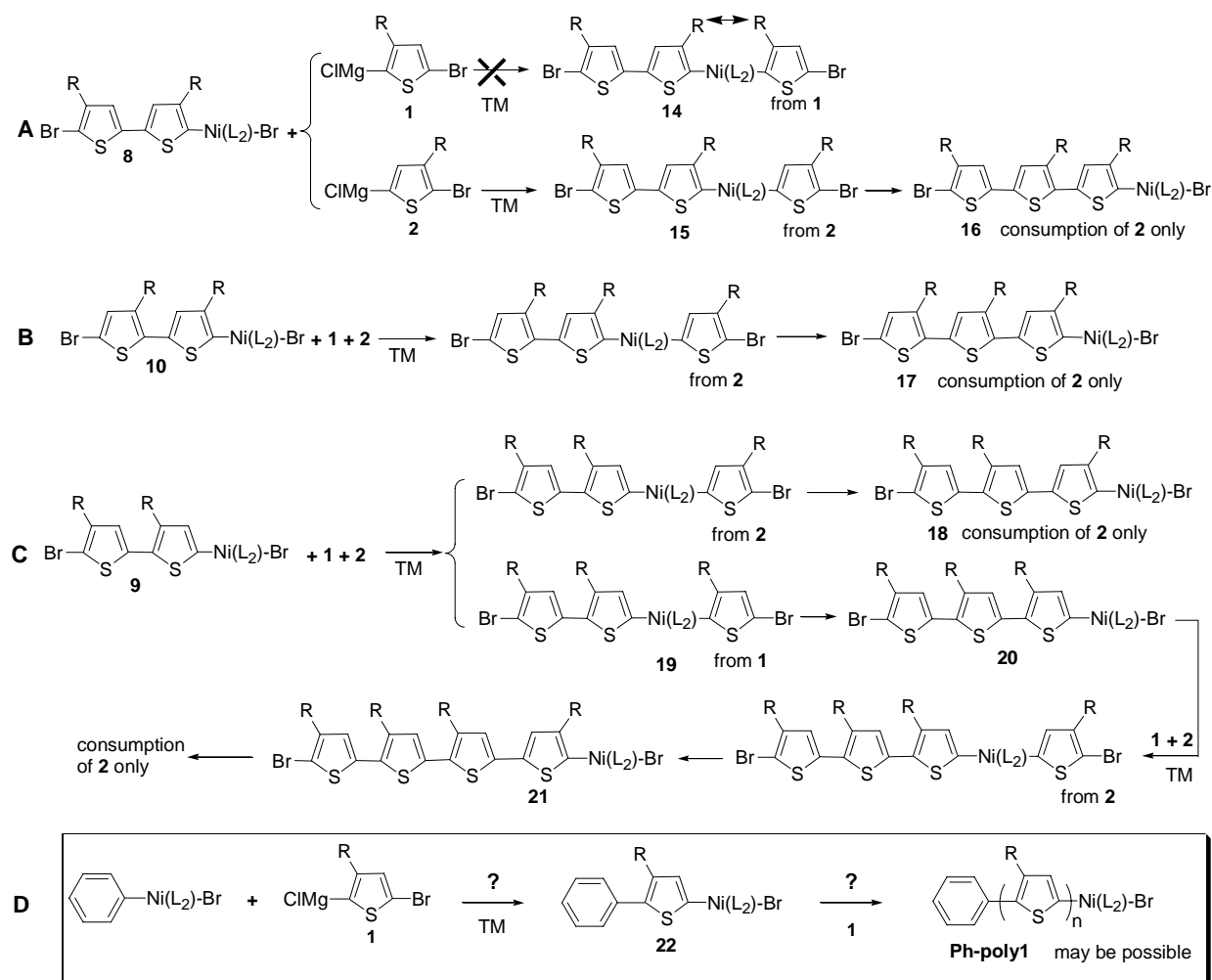
The monomer **1** in the presence of 3 % of **2** polymerized even slower with  $\text{Ph-Ni(dppp)-Br}$  initiator (30/1 ratio) than with  $\text{Ni(dppp)Cl}_2$ . Thus, only 14 % of the monomer mixture was converted within the first polymerization hour, 18 % for - 5 hours and 26 % - for 24 hours. Solid polymeric products of black color readily soluble in chloroform were isolated with yields of about 3, 7 and 10 % for those fractions, respectively. Detailed NMR analysis of the reaction product shed a light on the reaction of  $\text{Ph-Ni(dppp)-Br}$  and **1** contained 3% of **2** (30/1 monomer/initiator ratio). The following facts are noteworthy:

- 1) a near complete transfer of the Ph-group from the initiator into oligomeric and polymeric fraction was found by the integration of signals of the Ph-moiety to all thiophenic signals (both polymers and unreacted hydrolized monomers) for crude polymerization mixture. It should be taken into account that  $\text{Ph-Ni(dppp)-Br}$  species which do not couple with the monomer give easily volatile benzene after hydrolized of the polymerization mixture and therefore should not be observed in NMR spectra.

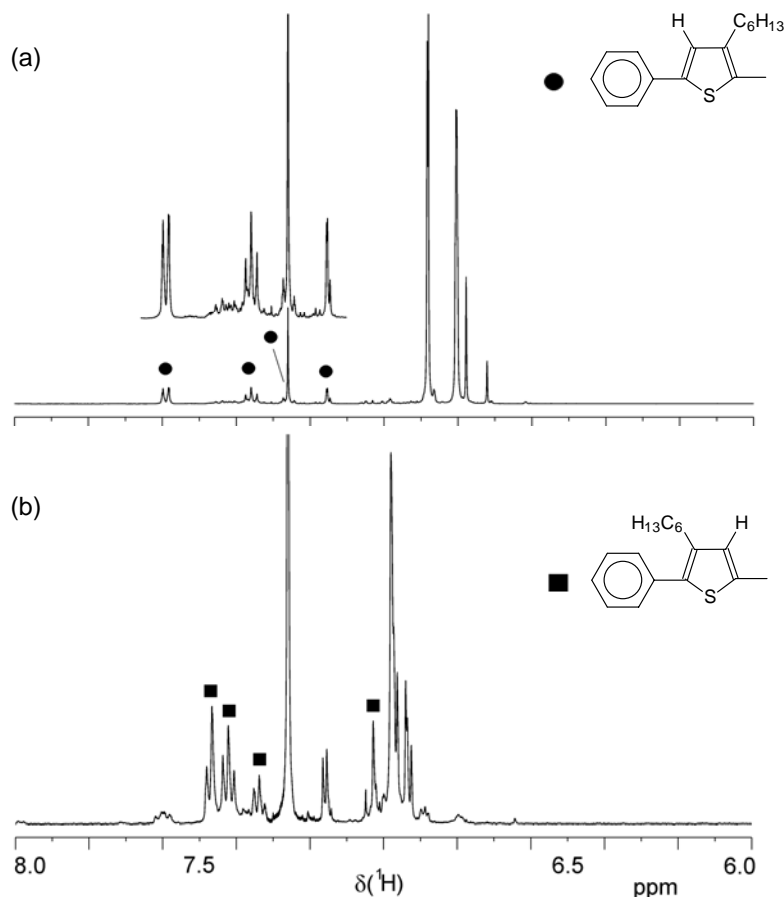
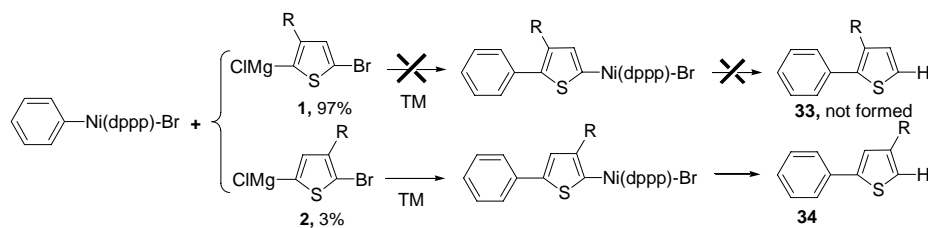
- 2) Second, integration of the starting and end groups of the solid polymeric product reveal that virtually all P3HT chains are Ph-terminated (which means that all P3HT formed was initiated by Ph-Ni(dppp)-Br). Furthermore, it is also seen that the first thienyl ring in the obtained solid P3HT is connected with the starting Ph-group in such a way as it expected for the coupling of the reversed monomer **1** (as shown in Figure 3 of the main text).
- 3) An important information brings a methanol-soluble fraction of the reaction mixture (Figure S4a). Besides a large amount of unreacted hydrolized monomers (since very low monomer conversion was observed in this experiment even at prolonged reaction) this fraction contains short thienyl oligomers (DP = 1 or 2) having Ph-starting group. It is important that Ph-group in those oligomers is connected to the first thiophene ring in a way as expected for the coupling of the regular monomer **2** (compound **34**, Scheme 4 of the main text), i.e., in the way different compared to the connection observed in the polymeric fraction of the same polymerization mixture (Figure S4b). In a number-average representation (but not in the weight-average one), this oligomeric Ph-Th(R)-fraction is a dominating one compared to the polymeric Ph-(R)Th-fraction. This further means that Ph-Ni(dppp)-Br initiator was predominantly coupled with the minority monomer **2** and converted Ph-Ni(dppp)-Br into sterically hindered initiator that is unable to initiate **1**. Since in this experiment the content of **2** was ~3 % and the monomer was added in 30-fold excess relative to the initiator, near all imitator species may be passivated if they selectively couple with **2**. In fact, polymerization of major monomer **1** (resulting into solid polymer with the yield below 10%) was initiated by the minority fraction of Ph-Ni(dppp)-Br that succeeded to couple with **1** and that was not deactivated further by the coupling with the rest of the monomer **2**.



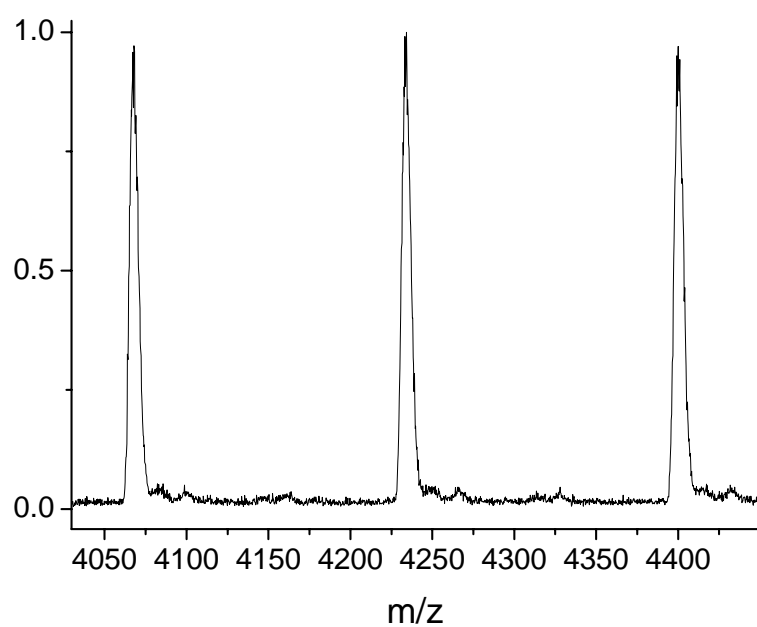
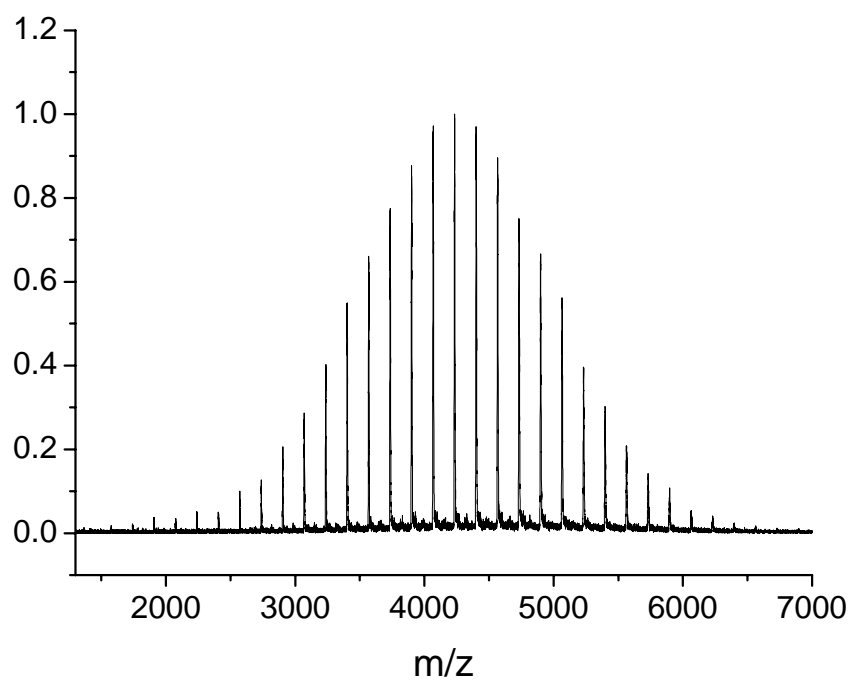
**Scheme S1.** (A, B) An explanation of why monomer **2** is selectively consumed from the mixture of **1** and **2** upon GRIM polymerization into regioregular HT P3HT.<sup>1,2</sup> (R = Hex) (C) A prediction that monomer **1** in the absence of monomer **2** could be polymerized into regioregular HT P3HT by the action of appropriate initiators having no alkyl substituents in the “*ortho*”-position to Ni, e.g., by the complex formed from Ni(L<sub>2</sub>)Cl<sub>2</sub>, **2** and **1**, or by externally added Ph-Ni(L<sub>2</sub>)-Br. (D) A prediction that polymerization of monomer **1** may be possible via initiation by sterically nonhindered Ph-Ni(L<sub>2</sub>)-Br.



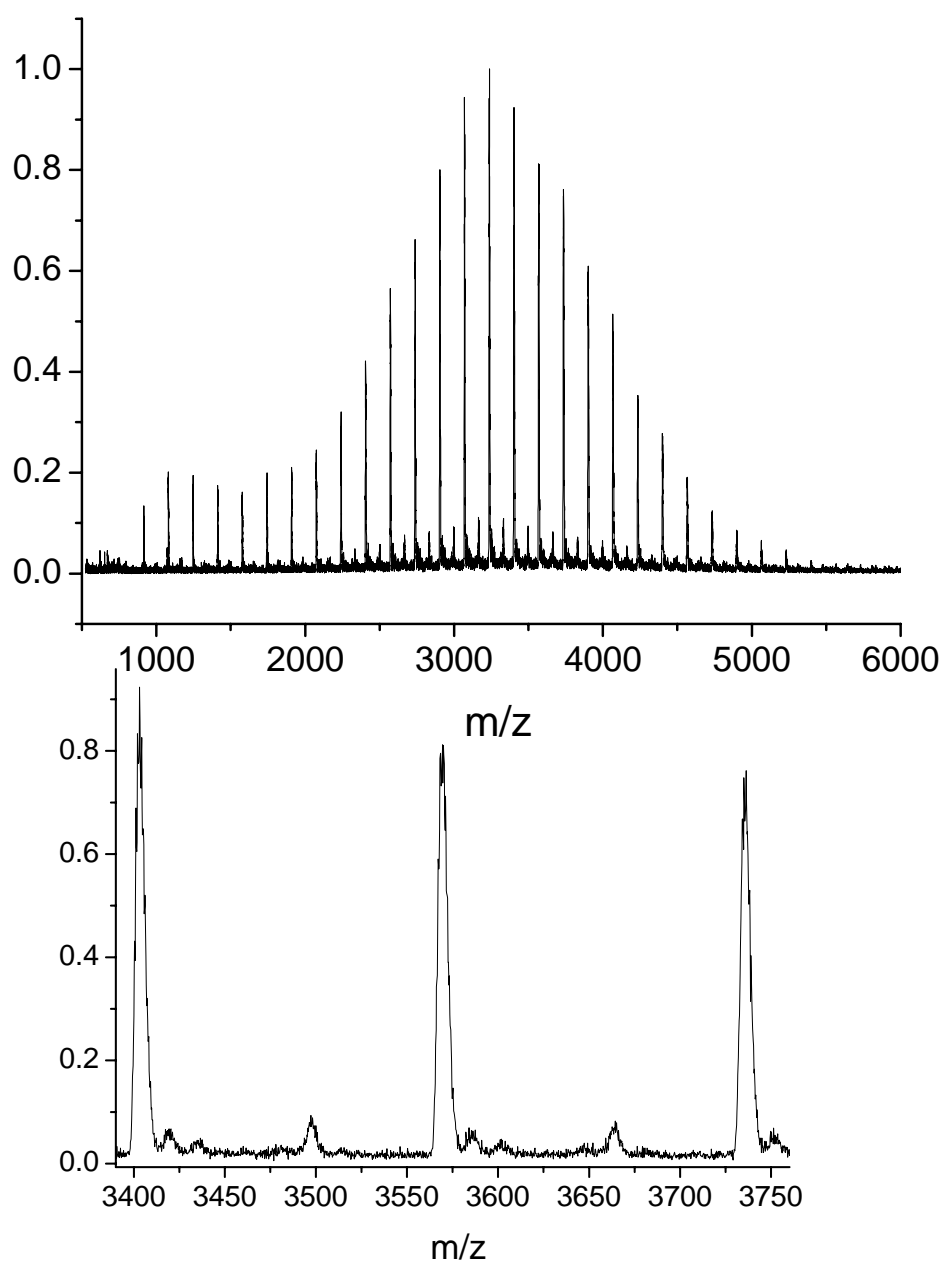
**Scheme S2.** An explanation of why polymerization of **1** initiated by Ph-Ni(dppp)-Br is suppressed if monomer **2** is also present in the reaction mixture in quantities sufficient to fully consume the initiator.



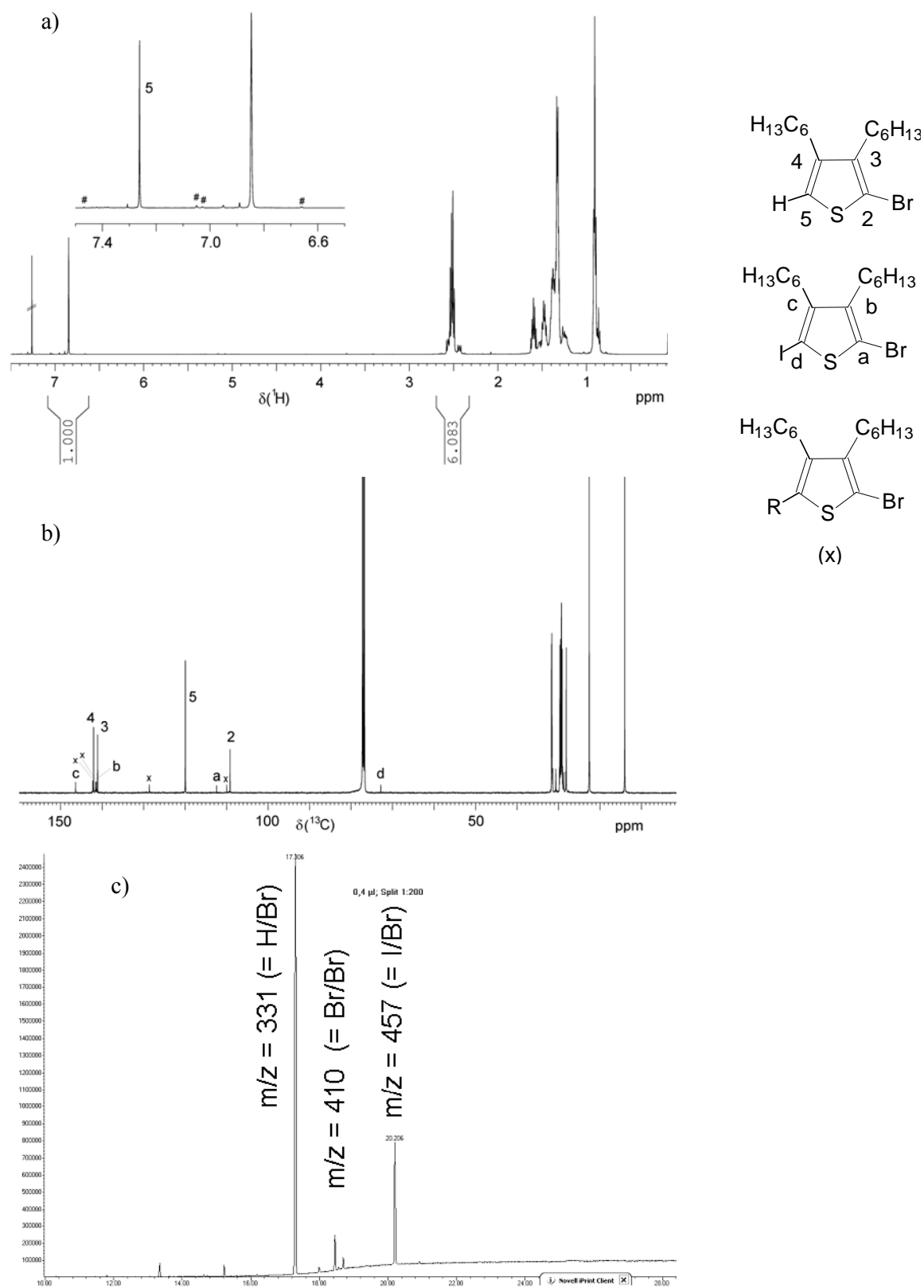
**Figure S4:**  $^1\text{H}$  NMR spectra: (a) of the methanol fraction of Ph-Ni(dppp)-Br-initiated polymerization of **1** contained 3% of **2** at 30/1 monomer/initiator ratio; polymerization time 5 hours; (b) of the polymeric product from the same reaction. The methanol fraction (Figure S4a) represents predominantly hydrolyzed monomer **1** (because of incomplete conversion in this particular experiment), but signals from the Ph-starting group (filled circles) attached to hexylthiophene as shown in picture (inset to figure a) are also seen. Noteworthy, this type of starting groups corresponds to the coupling of the minority monomer **2** with the initiator, but not with the monomer **1**. The fact that there is almost no starting groups with such type of connection are observed in the high MW fraction (Figure S4b) says that the initiator species which were reacted with **2** (represents the major pathway for consumption of the initiator Ph-Ni(dppp)-Br) were not active to polymerize further and reach high MW fraction. Instead, only those chains reached high MW which propagated from species formed upon the coupling of the initiator with the monomer **1** (this end-group type is marked by filled squares). Noteworthy, these species represent the minor pathway for consumption of the initiator Ph-Ni(dppp)-Br which explains the formation of much higher MW P3HT than may be expected from the monomer-to-initiator ratio.



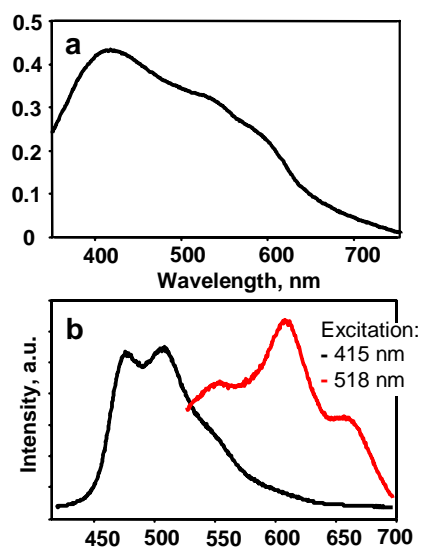
**Figure S5:** MALDI-TOF spectra of Ph/H terminated P3HT obtained upon polymerization of reversed monomer **1** by Ph-Ni(dppe)-Br.



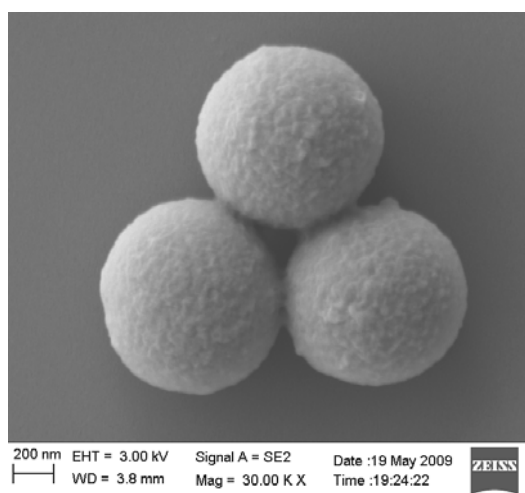
**Figure S6:** MALDI-TOF spectra of Ph/H terminated P3HT obtained upon polymerization of reversed monomer **1** by Ph-Ni(dppp)-Br.



**Figure S7:** (a)  $^1\text{H}$  and (b)  $^{13}\text{C}$  NMR spectrum of quenched polymerization mixture of the monomer **3** in the presence of  $\text{NidppeCl}_2$  (solvent:  $\text{CDCl}_3$ ). Signals marked with # are  $^{13}\text{C}$  satellites. (c) Gas chromatogram of this mixture with  $m/z$  values of the main peaks and substituents in 2- and 5- position. These data confirm that neither polymerization nor oligomerization of **3** occur of  $\text{NidppeCl}_2$ . (Similar results were obtained with  $\text{NidpppCl}_2$ ,  $\text{Ph-Nidppe-Br}$  and  $\text{Ph-Nidppp-Br}$ ).



**Figure S8.** (a) UV-vis (a) and fluorescence (b) spectra of the dispersion in  $\text{CHCl}_3$  of low molecular weight PT obtained via KCTP using  $\text{Ni}(\text{dppe})\text{Cl}_2$  initiator.



**Figure 9.** SEM images of the submicron organosilica particles after modification with PT via SI-KCTP.

**Scheme S3.** Graft copolymerization of **2a** and **4** from organosilica particles via SI-KCTP.

