An Efficient and Reliable Procedure for the Preparation of Highly Reactive Rieke Zinc

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Abstract: Rieke zinc has a wide potential for applications in organic chemistry, notably for the synthesis of highly chemoselective organozinc reagents. However, due to the rather unreliable preparation method, leading to large batch to batch variations, its use has been rather limited. Rieke zinc is commonly prepared by the reduction of zinc chloride with lithium using a stoichiometric amount of naphthalene. In our hands, it was observed that the reaction outcome was highly dependent on the naphthalene source and purity grade. The presence of benzothiophene seems crucial to avoid coagulation of the zinc particles and the amount of benzothiophene has a large effect on the physical properties and the reactivity of the resulting zinc powder. Accordingly, highly reactive Rieke zinc was easily prepared from zinc chloride by adding an optimum amount (3 mol% with regard to ZnCl₂) of benzothiophene into the lithium naphthalenide solution (prepared in situ). The Rieke zinc obtained in this way was successfully employed in the so-called "Rieke method" to prepare regioregular poly(3hexylthiophene) (P3HT). The novel approach enables preparation of Rieke zinc in a reproducible manner, which considerably facilitates its use in both small molecule and polymer synthesis.

Keywords: benzothiophene; naphthalene; poly(3-hexylthiophene) (P3HT); reproducibility; Rieke zinc

Organozinc compounds are important synthetic intermediates as they exhibit excellent chemoselectivity and good functional group tolerance and stability.^[1] However, due to their lower reactivity towards a broad range of electrophiles and moderate yields compared to Grignard reagents, they have received rather limited attention, mostly for Reformatsky^[2] and Simmons–Smith reactions.^[3] The first organozinc compound to be reported by Frankland in 1849 was prepared from the reaction of metallic Zn with ethyl iodide.^[4] However, due to the lack of reactivity of the Zn metal, this reaction was quite limited in its scope. Several methods have been used to activate Zn, such as washing with a hydrochloric acid solution^[5] or adding 1,2-dibromoethane to prevent passivation of the zinc surface.^[6] In spite of these methods, direct oxidative addition of the Zn metal was only successful for relatively reactive alkyl iodides. Thus, metallic Zn did not generally allow preparation of organozinc reagents directly from organic halides. In the early 1970s, Rieke et al. introduced a new method which utilized potassium metal to reduce zinc salts, affording highly reactive Zn metal powder.^[7] This active form of Zn was called "Rieke zinc (Zn*)" and displayed excellent reactivity towards organic halides compared with bulk Zn metal, Zn dust or metallic Zn activated by entrainment methods. Later on, in 1991, the same group reported on an alternative method to prepare the active Zn species under milder and safer conditions by reduction of the zinc salt with lithium in the presence of naphthalene as an electron carrier, giving rise to even more reactive Zn*.^[8] Reduction of a zinc cyanide salt by the same method resulted in Rieke zinc which reacts at a synthetically useful rate with alkyl or aryl chlorides at room temperature to produce the corresponding organozinc halide reagents.^[9] Liquid ammonia has also been used as an electron carrier to produce active Zn powder.^[10] Since then,

Rieke zinc has found application in numerous organic syntheses, mostly for the preparation of organozinc reagents. Compared to Grignard and organolithium reagents, organozinc derivatives tolerate the presence of a wide range of functional groups, such as ketones, nitriles, esters and other halides, making it a very useful synthetic tool.^[11] Rieke zinc has also been used as a reducing agent for common functional groups (conjugated aldehydes, alkynes, esters and nitro compounds).^[12]

In polymer synthesis, the "Rieke method" - referring to the synthesis of regioregular (fully head-to-tail coupled) poly(3-hexylthiophene) (P3HT) (co)polymers by reaction of 2,5-dibromothiophene monomers with Rieke zinc – is of high relevance, as the resulting semiconducting conjugated polymer materials are of great importance in organic electronics, notably in organic photovoltaics.^[13,14] Side chain functionalized poly(3-alkylthiophenes) were also prepared by the same protocol,^[15] and the method was extended to a limited number of other polyarylenes such as $poly(p-phenylene)^{[16]}$ and poly(dialkylcyclopentadithiophene)^[17]. Besides these notable exceptions, the Rieke polymerization protocol has been almost absent from literature. Thiophene-based homopolymers are generally prepared by the Grignard metathesis (GRIM) method,^[14] although this procedure is not compatible with all desired functional side chain patterns (e.g., esters).[15]

Upon closer inspection of the available literature, one notices that the applicability of Rieke Zn seems mainly limited by obstacles in its preparation, which later on have a profound effect on the reactivity. Kharisov et al. have prepared the active Zn metal in a complicated and completely closed system.^[18] Vyvyan et al. reported some difficulties in preparing large quantities of alkylzinc reagents due to batch to batch variations in the reactivity of the Rieke zinc metal.^[19] Zhou attempted to prepare alkylzinc bromides from commercially available Rieke zinc (Aldrich), but this did not lead to high conversion of the primary alkylzinc bromides, even when a large excess of the active Zn metal was used.^[20] He also tried to prepare the active Zn metal with Li and a stochiometric amount of naphthalene, following the procedure from Rieke et al.,^[8] which also gave no improvement.

In this paper, we report on a simple preparation method for highly reactive Rieke zinc under common laboratory conditions. As a proof of principle, the improved synthetic procedure was applied for the preparation of both 3-hexylthiophene and P3HT.

The highly reactive form of metallic Zn, generally referred to as Rieke zinc (Zn*), was first prepared in 1973.^[7] The synthetic protocol involved reduction of a zinc salt in refluxing THF or DME utilizing either Na or K. These highly reactive Zn powders showed high reactivity towards organic halides in oxidative

addition reactions. On the other hand, Rieke zinc prepared by this procedure was successfully implemented in Refortmatsky reactions at room temperature or below, affording quantitative reaction yields.^[21] Later on, a safer and milder procedure which uses Li and a catalytic amount of naphthalene (10 mol%) was introduced.^[8,22] Initially it was believed that the use of an additional electron carrier would complicate purification of the final organic products, but actually the electron carrier can easily be removed by washing the reactive Zn powder with fresh THF or DME. Moreover, the preparation in THF or DME using either a stochiometric amount of lithium naphthalenide^[8] or Li and a catalytic amount of naphthalene even led to active Zn of higher reactivity. Reduction of the zinc salt with Li and naphthalene requires vigorous stirring for about 10 h to obtain the active Zn slurry, but also to prevent the reduced Zn to coat the Li surface and thereby inhibit the reduction. The most convenient method actually involves reduction of the zinc salt with a stoichiometric amount of lithium naphthalenide, shortening the reduction time and eliminating the coating problem. The procedure is carried out in two steps. In the first step, the lithium naphthalenide/THF solution is prepared, which takes about 2 h. In the next step, the solution of the zinc salt in THF is transferred using a cannula into the lithium naphthalenide/ THF solution over 10-15 min. When stirring is stopped, the very finely dispersed zinc particles settle out, leaving a clear colorless supernatant above the Zn powder. In some cases, the supernatant may appear more or less green due to the presence of some lithium naphthalenide. This method, with some improvements as mentioned below, was utilized for the preparation of the highly reactive Rieke zinc metal powder during this study.

In the standard preparation of highly reactive Rieke zinc, naphthalene is used as an electron carrier.^[8] However, when we started to conduct Rieke polymerization reactions (towards P3HT) with new sources of naphthalene, the *in situ* formed Zn metal particles were found to strongly coagulate, yielding chunky metal clusters. On the other hand, the "old" naphthalene batch (Merck) still gave the desired Rieke zinc as a finely dispersed black slurry. Hence, it became clear that the old naphthalene had to be somehow different compared with the new one, and a number of analytical methods was applied to achieve insight on the properties (notably the impurities) of different naphthalene sources.

Commercially available naphthalene, produced from coal tar (of which it is the most important polycyclic aromatic hydrocarbon fraction),^[23] contains small amounts of sulfur-containing aromatic compounds. The most abundant among these impurities is benzothiophene (BT), as previously also observed by Hiyoshi et al.^[24] In spite of the fact that the thia-heterocycles are normally eliminated by a desulfurization process, it is quite difficult to remove them to a full extent. Consequently, commercial naphthalene generally contains small amounts of thia-aromatic impurities.

The metallic trace elements in the naphthalene samples and in the Rieke zinc powder were initially analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) for almost all the elements of the periodic table. Only a trace of sulfur was detected. In addition, high-performance liquid chromatography (coupled to a fluorescence detector; HPLC-FLD) analysis of the old (Merck) and new (Acros) naphthalene was performed. The contaminant gave a signal around 230 nm. The HPLC results obtained for the two different naphthalene samples are summarized in Table 1. Analysis showed that both of samples contained the same contamination. The amount was, however, nine times higher in the old batch compared to the new naphthalene.

To identify the exact nature of the main contaminant, gas chromatography-mass spectrometry (GC-MS) analysis was performed on four different naphthalene batches (Table 2). According to this analysis, the main contaminant has a molar mass of 134 gmol⁻¹, which (as expected) corresponds to BT. Additionally, the mass spectrum of the contaminant was in accordance with the spectrum of BT under the same conditions. The values obtained from GC-MS were somewhat lower than the HPLC-FLD ratios due to the difference in response factor.

From the above, it is clear that the old (Merck) naphthalene was contaminated with BT to a larger extent and apparently this has an effect on the stabilization of the Zn particles in THF solution and hence on the success of the Rieke zinc preparation and reactivity. For this reason, we have pursued a convenient

Table 1. Contaminant content in different naphthalene sources, as determined by HPLC (relative response).

Naphthalene	Purity [%]	Impurity content [%]	Exact purity [%]
Old (Merck)	99+%	5.6	94.4
New	99+%	0.6	99.4
(Acros)			

Table 2. Benzothiophene content in different naphthalene sources, as determined by GC-MS (relative response).

Naphthalene	Purity [%]	BT content [%]
Old (Merck)	99+%	1.69
Merck	$\geq 99\%$	0.06
Aldrich	$\geq 99\%$	0.14
New (Acros)	99+%	0.20



Scheme 1. Optimized procedure for the preparation of Rieke zinc.

procedure for the preparation of Rieke zinc in highly active form by reducing the zinc chloride salt in THF with lithium naphthalenide (prepared *in situ*) and deliberate addition of a catalytic amount of BT, as shown in Scheme 1.

It appears from our analysis that the presence of a catalytic amount of BT in the reducing lithium naphthalenide solution is crucial, affording a fine dispersion of the reactive metal powder. Without BT, coagulation of the Zn metal particles occurred, giving rise to unreactive chunky metal clusters. According to Rieke et al., the appearance of the formed active Zn powder depends on the amount of zinc chloride salt added into the lithium naphthalenide solution and on the addition speed.^[8] With slow addition, i.e., 3 seconds per drop with no excess of Zn, a finely divided black slurry of the active Zn is formed, whereas in case of fast addition, i.e., ~1 second per drop, spongeshaped active Zn is obtained. This effect was also observed by Bronk and discussed in his dissertation on C-C bond formation via intramolecular conjugate addition of organozinc compounds.^[25] In our hands, however, it appeared that the reason of the coagulation of the highly reactive Zn particles was neither the addition of an excess of zinc chloride salt nor the addition speed, but the phenomenon could be attributed to the BT impurity, which is present in naphthalene in tiny but varying quantities.

At this stage, a number of additional experiments was conducted to optimize the Rieke Zn formation. First, naphthalene with different purity grades from different companies was purchased and the reduction process was carried out in parallel with reactions employing the old (Merck) naphthalene to allow full comparison. All experiments that were performed with new naphthalene batches initially failed. Since the major difference between the naphthalene samples was the BT content, novel reactions were conducted with addition of some pure BT to the lithium naphthalenide mixture. Upon addition of the zinc chloride solution to lithium naphthalenide containing BT, a fine slurry of the highly reactive Rieke zinc metal powder was obtained. Further studies revealed that the amount of BT had a large effect on the physical properties of the resulting reactive metal powder, which then later on affects the oxidative addition pro-

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Figure 1. SEM-EDX pictures of the Rieke zinc powder prepared with old (Merck) naphthalene (*left*), 1.5 mol% BT (*middle*), and 3 mol% BT (*right*) (see EDX figure in the Supporting Information).

cess of the Rieke zinc metal to organic halides. Thus, several experiments were carried out to optimize the ratio BT/zinc chloride. It was found that the optimum amount of BT to be added is 3 mol% (with respect to ZnCl₂). The limiting amount to prevent coagulation seems to be 1 mol%.

Scanning electron microscopy-energy disperse Xray spectroscopy (SEM-EDX) studies were conducted on the Rieke metal powder prepared with the different methods to study the impact of the addition of BT on the formed Zn metal powder (Figure 1). In case of 1.5 mol% of BT (Figure 1, *middle*), the obtained Zn powder was not homogeneous and contained Zn particles of very different size compared with the ones prepared with either the old (Merck) naphthalene (Figure 1, *left*) and the naphthalene containing 3 mol% of BT (Figure 1, *right*).

The Zn metal powder obtained from the reaction with 1.5 mol% BT was implemented in a reaction with 2,5-dibromo-3-hexylthiophene (5) (towards the formation of P3HT). As expected, oxidative addition of the Rieke zinc did not proceed to a full extent (as analyzed by ¹H NMR). This can be related to the decreased active surface of the reactive metal by agglomeration of the formed small particles, which gives rise to a loss of their reactivity towards organic halides. However, when we prepared the Rieke zinc by adding at least 3 mol% of BT into the lithium naphthalenide solution, we always obtained a fine black slurry of Rieke Zn metal, showing excellent reactivity in the oxidative addition towards organic halides. Additionally, the active Zn powder kept its reactivity over several days and no further agglomeration of the particles (that could lead to loss of reactivity) was observed.^[26] In spite of the fact that the mechanism of the stabilization of the Rieke zinc particles as a fine dispersion in THF supernatant is not fully understood, one could suggest a possible complex formation of BT with either Li or zerovalent Rieke Zn.^[27,28]

Following Rieke et al., we then demonstrated the excellent reactivity of the Rieke zinc powder pre-

pared through our optimized procedure by utilizing it in the well-known synthesis of P3HT.^[14,29,30] The preparation of P3HT starts from the readily available reagents 3-bromothiophene (**3**) and hexyl bromide (**1**). Their conversion to 2,5-dibromohexylthiophene (**5**) is depicted in Scheme 2.

First, hexyl bromide (1) was treated with an excess of Rieke Zn*. The reactive Rieke Zn metal readily undergoes oxidative addition in a 1.0-1.2 Zn*/RX molar ratio at room temperataure to afford hexylzinc bromide (2) within $2 h.^{[8]}$ The hexylzinc bromide (2) solution was dark brown in color and stable under an argon (Ar) atmosphere, and the conversion was estimated to be >99%, as determined by GC-MS (after quenching with an iodine solution). The excess of the reactive metal powder could easily be separated from the solution by allowing the Zn to settle down for about 3 h. The hexylzinc bromide (2) solution was then transferred via cannula to another flask for the next reaction. In the latter, the coupling was conducted by reaction of n-hexylzinc bromide (2) with 3-bromothiophene (3) in the presence of 5 mol% of Ni(dppe)Cl₂ {[1,2-bis(diphenylphosphino)ethane]nickel (II) chloride].^[31] 3-Hexylthiophene is usually prepared via Kumada coupling of 3-bromothiophene using a Grignard instead of an organozinc reagent. To the best of our knowledge, Rieke chemistry was employed here for the first time to prepare 3-hexylthiophene. The coupling reaction was performed at room temperature overnight. Additionally, when the cou-



Scheme 2. Preparation of 2,5-dibromo-3-hexylthiophene (5) employing Rieke zinc.



Scheme 3. Regio-controlled synthesis of P3HT.

pling reaction was performed in the presence of LiBr the reaction time could be shortened from 2 days to 18 h and the yield was dramatically enhanced from 42 to 82% (close to the 87% reported for the Kumada coupling of the corresponding Grignard reagent).^[31,32,33,34] Until now, the role of the LiBr is not fully understood. Nonetheless, the beneficial effect of the addition of a Li salt in such reactions is well documented. Koszinowski and co-workers suggested that the Li salt forms complexes with the organozinc species, which increases their solubility and provides a clean metal surface. On the other hand, due to the electronegativity of the halogen atom, the organozinc gains nucleophilic character.^[35] Subsequently, bromination of 3-hexylthiophene with N-bromosuccinimide (NBS) under mild conditions gave 2,5-dibromo-3-hexylthiophene (5).^[34] Simple distillation of the crude product vielded the monomer in high purity.

The synthesis of regionegular P3HT (7) is shown in Scheme 3. The highly reactive Rieke zinc (Zn*) metal powder undergoes oxidative addition to 2,5-dibromo-3-hexylthiophene in a regiospecific manner, yielding 2-bromo-5-(bromozincio)-3-hexylthiophene (6a) as the major (95%) and 2-(bromozincio)-5-bromo-3-hexylthiophene (6b) as the minor regioisomer (5%). The regioselectivity of the oxidative addition of Zn* metal is higher at lower temperature.^[29] In our case, the total yield for both regioisomers was >99%, as confirmed by GC-MS analysis after quenching the crude reaction mixture with a saturated ammonium chloride solution. After completion of the reaction, stirring was stopped and unreacted Zn* particles were allowed to settle down. Removal of the excess Zn* is crucial since it can further react with a bromine source and give rise to bis(organozinc) products, which lead to low molecular weight species. Polymerization of the resulting organozinc solution was carried out by adding a catalytic amount of Ni(dppe)Cl₂ catalyst to afford highly regioregular P3HT.^[13]

After completion of the reaction the polymer was precipitated in a solution of 2M HCl/MeOH (2:1). The yield of the polymerization was over 90% at this point. The molecular weight and corresponding polydispersity were measured by gel permeation chromatography (GPC) in THF. The polymer before extraction had $M_w=24.3 \times 10^3$ and $M_n=6.8 \times 10^3$ (corresponding to 41 repeating units per chain) with a polydispersity D=3.6. The crude polymer was then purified by means of sequential Soxhlet extractions with methanol and hexanes (24 h each), removing residual monomer and oligomer fractions. The yield was about 70% after Soxhlet purification, and the molecular weight increased to $M_w = 36.1 \times 10^3$, $M_n = 22.9 \times 10^3$ (corresponding to 138 repeating units per chain), while the polydispersity narrowed down to 1.6. Therefore, one can conclude that the monomers were quantitatively cross-coupled in the polymerization reaction with at least 70% of the monomers incorporated in the polymer fraction.

The optimized Rieke procedure was later on also applied towards the preparation of a number of esterfunctionalized P3AT copolymers, of particular interest for organic solar cell applications, and also there decent molecular weights were routinely obtained with high reproducibility.^[15e-i]

In summary, we have developed a straightforward procedure to prepare Rieke zinc in highly reactive form under standard chemical laboratory conditions. The key to afford a highly reproducible protocol is the addition of a particular amount (3 mol%) of BT – which was identified as the main additive responsible for previously observed batch to batch variations - to the lithium naphthalenide solution employed for zinc chloride reduction. The reactivity of the newly prepared active Zn powder was demonstrated in the oxidative addition to hexyl bromide and 2,5-dibromo-3hexylthiophene to give the corresponding organozinc reagents in excellent yields. The optimized method also readily enables the preparation of active Rieke Zn in large quantities with high reproducibility. Accordingly, we believe that this optimized procedure can increase the synthetic scope of Rieke zinc in both general organic and polymer chemistry, as was already shown recently by the preparation of polythiophene-based conjugated (co)polymers for applications in organic photovoltaics.[15e-i]

Experimental Section

Materials and Methods

All manipulations were carried out with the aid of a dual manifold vacuum/Ar system. Lithium (granular, 99+%) from Acros was stored in a Schlenk tube under Ar. Lithium, naphthalene and benzothiophene (Sigma–Aldrich, 98%) were weighed in air as needed and transferred to the Schlenk tube under a stream of Ar. Naphthalene with different purity grades was purchased from different suppliers

and each stored in a separate dessicator together with BT over P_2O_5 . Zinc chloride (Acros, analysis grade 98,5%) was transferred into small vials in the glove box and stored in a dessiccator over P_2O_5 . Zinc chloride was dried by treating it with thionyl chloride and heating with a Bunsen burner, and subsequently removed under a stream of Ar. THF was freshly distilled from Na/benzophenone under an N₂ atmosphere at atmospheric pressure prior to use. Brass cannulas were stored at 110°C and cleaned immediately after use with acetic acid (in the case of Zn* remnants), acetone (to clean non-polymeric residues), or hot chloroform and/or chlorobenzene (for polymer-based contaminations).

HPLC analysis was carried out using an Agilent 1100 series system incorporating a chrompack 150 mm × 4.6 mm column and a spectra SYSTEM FL2000 type fluorescence detector. The mobile phase was MeCN/water (53/47 to 100/0 v/v) with a flow rate of 1.6 mLmin⁻¹ and an injection volume of 20 µL. SEM was performed with an FEI Quanta 200 FEG-SEM in combination with EDX. ELAN DRC-e. ICP-MS was employed to analyze the metallic trace elements in naphthalene. GC-MS analysis was carried out with a thermoquest TSQ7000, applying a DB-5MS $30 \text{ m} \times$ 0.25 mm column, in the temperature range 35-320 °C. Molecular weights and molecular weight distributions were determined relative to polystyrene standards by GPC. Chromatograms were recorded on a Spectra Series P100 (Spectra Physics) equipped with two mixed-B columns (10 µm, 0.75 cm × 30 cm, Polymer labs) and a refractive index detector (Shodex) at 40 °C. THF was used as the eluent at a flow rate of 1.0 mLmin^{-1} .

Enhanced Preparation Method for the Highly Reactive Rieke Zinc (Zn*) Metal Powder

Two 120-mL Schlenk vessels, A and B, were dried by heating with a Bunsen burner under reduced pressure and cooled down to room temperature under a stream of Ar. Schlenk vessel A, filled with Ar, was weighed and then reassembled to the Schlenk line. Under a stream of Ar, ZnCl₂ was charged to the vessel. After three Ar/vacuum cycles, ZnCl₂ was wetted with a small amount of SOCl₂. The Schlenk vessel was heated by a Bunsen burner until the ZnCl₂ salt melted and a white fume was released, and the Schlenk flask was then cooled down under an Ar flow. Schlenk flask A was weighed again to determine the exact amount of ZnCl₂ and a stirring bar was added. Dried ZnCl₂ (1.1 equiv.) was dissolved in freshly distilled THF (25 mLg^{-1}) . Li pellets (2.2 equiv.), naphthalene (2.25 equiv.) and benzothiophene (0.04 equiv.) were weighted in air and charged into Schlenk vessel B under an Ar stream. Dry THF (the same amount as added to dissolve ZnCl₂) was added and the solution turned from colorless to dark green within less than 2 min. It was stirred further for 2 h to dissolve the Li pellets. The ZnCl₂ solution was transferred dropwise via cannula to the lithium naphthalenide solution over 10-15 min. The resulting black suspension might be stirred for 1 more h to consume the remaining Li or stirring can be stopped right after the addition. The highly reactive zinc powder was allowed to settle down for a couple of hours. The supernatant was siphoned off via cannula leaving the Zn* powder. The thus prepared Rieke zinc was ready to use.

Synthesis of 3-Hexylthiophene (4)

Hexyl bromide (4.7 mL, 28.1 mmol) was dissolved in dry THF (40 mL) and added via a cannula to the active zinc powder (33.82 mmol) then the reaction mixture was stirred for 3 h at room temperature. Stirring was stopped and the solution was allowed to stand for a couple of hours to allow the excess of zinc to settle down from the dark brown organozinc bromide solution. In a 300-mL flame-dried Schlenk vessel, LiBr (3.41 g, 39.25 mmol), Ni(dppe)Cl₂ (0.94 g, 1.784 mmol), and 3-bromothiophene (2.5 mL, 26.76 mmol) were dissolved in dry THF (150 mL). The organozinc bromide solution was then transferred via cannula over a period of 1 h to this mixture under continuous stirring at room temperature and the reaction mixture was allowed to stir overnight. The resulting mixture was then quenched with saturated NH₄Cl, followed by extraction with diethyl ether, and simple distillation afforded 3-hexylthiophene as a colorless liquid; yield: 3.84 g (82%).

Synthesis of 2,5-Dibromo-3-hexylthiophene (5)

2,5-Dibromo-3-hexylthiophene was obtained by bromination of 3-hexylthiophene following the literature procedure as reported by Bäuerle et al.^[34]

Synthesis of Poly(3-hexylthiophene) (P3HT)

Α solution of 2,5-dibromo-3-hexylthiophene (4.08 g, 12.5 mmol) in THF (50 mL) was added via cannula to freshly prepared (according to the new procedure) Rieke Zn* (13.79 mmol) at -78 °C. The mixture was stirred for 1 h at this temperature and then allowed to warm to 0°C gradually. The unreacted Zn* was left to settle down overnight and the formed organozinc supernatant was then transferred by cannula via a 0.45 µm acrodisc filter into a flame-dried Schlenk tube. Via a cannula, 0.2 mol% of Ni(dppe)Cl₂ (0.013 g, 0.025 mmol) suspended in THF (5 mL) was added to the ice-cooled organozinc solution. The Schlenk vessel was immersed into a preheated oil bath at 60°C and the mixture was stirred at this temperature overnight. It was then poured into a solution of MeOH:HCl (2M) and the resulting dark precipitate was filtered off and washed several times with MeOH. The crude polymer $(M_w = 24.3 \times 10^3, M_n =$ 6.8×10^3 , D=3.6) was transferred into an extraction thimble and purification was performed by sequential Soxhlet extractions with MeOH, acetone and hexanes. The polymer was collected with CHCl₃ and the solvent was removed under reduced pressure. The polymer was redissolved in CHCl₃ and precipitation was again performed upon addition of MeOH. Filtration and drying under high vacuum afforded the pure P3HT material; yield: 1.44 g (70%); $M_{\rm w} = 36.1 \times$ 10^3 , $M_{\rm p} = 22.9 \times 10^3$, D = 1.6.

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