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On the 'True' Structure of Push-Pull Type Low Bandgap Polymers for Organic Electronics

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Donor-acceptor type conjugated polymers are a dominating class of active materials in the field of organic electronics. Their adjustable light-harvesting, charge transfer and charge transport characteristics are beneficially applied in organic photovoltaics, photodetectors and thin-film transistors. The conventional synthetic approach toward these push-pull polymers is based on Suzuki or Stille cross-coupling of complementary functionalized (hetero)aromatic monomers. In the ideal world, this gives rise to a perfect alternation of the employed building blocks throughout the polymer backbone and this alternation of electron rich (donor/push) and electron deficient (acceptor/pull) moieties leads to a substantial decrease of the bandgap. In recent years, however, it has become increasingly clear that the 'real' structure of the resulting alternating copolymers is often quite different from the projected one. Structural imperfections can for instance result from homocoupling of two identical building blocks. Furthermore, the polymer end groups are often also not those expected. In this progress report, we provide an overview of the recent literature observations of structural imperfections in push-pull conjugated polymers, the difficulties to observe them and their impact on device performance. The strong effect of homocoupling on material and (organic solar cell) device quality and reproducibility is particularly emphasized.

1. Introduction

Continuous research efforts over the past decades have led to an impressive progress in the field of organic semiconductors and a gradual improvement of their optoelectronic properties and the devices built from these materials.[1] This evolution has gone hand in hand with the development of new organic conjugated materials. When looking in particular to conjugated polymer semiconductors employed in organic photovoltaics (OPV's), one of the most popular application fields of these materials, they can, from a chronological point of view, essentially be divided in three main classes: i) poly(*p*-phenylene vinylene)s (PPV's), ii) poly(3-alkylthiophene)s (P3AT's) and iii) alternating donor-acceptor copolymers.[2–4] Specific synthetic protocols have been developed for each of these material classes. For PPV's and P3AT's (the most well-known example being P3HT or poly(3-hexylthiophene)), substantial efforts have been devoted to the preparation of well-defined, 'defect free' polymers (**Figure 1**). PPV's are typically synthesized via post-polymerization thermal conversion of a precursor polymer, for which several different routes exist (Wessling, sulfinyl, …), to the final conjugated PPV material.[5] Defects can be introduced in the conjugated backbone via incomplete elimination reactions, leading to inferior material properties and device characteristics.[5,6,7] Also for polythiophenes, the structural perfection of the conjugated backbone has gained large attention.[8,9] The asymmetric nature of the monomers used for the preparation of P3AT's results in three different coupling patterns of two adjacent monomer units: head-to-tail (HT), tail-to-tail (TT) and head-to-head (HH). HH coupling results in a twist of the conjugated backbone, limiting the conjugation length and altering the optoelectronic and physicochemical properties (e.g. the (semi)crystallinity). This topic received a lot of attention, which led to the development of optimized synthetic protocols allowing the preparation of P3AT's with >95% regioregularity, such as the Kumada catalyst transfer condensative polymerization (KCTCP, commonly known as the Grignard metathesis polymerization (GRIM)).[10] Besides the conjugated backbone, the polymer end groups of both classical material classes have also been investigated in detail. Especially for P3AT's, end-group analysis has often been performed to gain insight in the mechanistic aspects of the controlled, 'living' character of the KCTCP. When this type of reaction proceeds in a controlled fashion, eliminating all transfer and termination reactions, all polymer chains are end-capped with H/Br groups.[10,11] The bromide end groups can then be employed for further post-polymerization reactions.[12–14] For PPV's, there are less examples of detailed end-group analysis, partly because of the high molar masses typically obtained for these materials, complicating structural analysis. Via in-depth NMR studies, Adriaensens et al. found indications for carbonyl-type end groups (aldehydes and carboxylic acids), attributed to reactions between oxygen and the radical ends of the polymer chains.[6]

To date, however, PPV's and P3AT's have become of less importance for organic electronics (notably photovoltaics) as they are outperformed by the more recent class of push-pull or donor-acceptor type copolymers.[4] The optoelectronic and film forming properties of these push-pull conjugated polymers can readily be tuned by choosing the appropriate constituent building blocks and (solubilizing) side chain patterns to meet the specific requirements of each application. For OPV's for instance, it is crucial to combine a low bandgap (to maximize light harvesting) with optimized energy level alignment (to achieve efficient charge transfer from the electron donor to the electron acceptor component combined in a bulk heterojunction photoactive layer).[15] Furthermore, the processability and miscibility of the conjugated polymer with the electron acceptor component (historically mostly fullerenes) is crucial for the device outcome as well.[16,17]

Somewhat surprisingly, the prevalence of structural defects in the conjugated polymer backbone of this type of materials has received very little attention, although negative effects of structural imperfections on the final device output can be foreseen. The main reason for this can be found in the nature of the synthetic protocols employed for push-pull type conjugated polymers. Whereas the polymerization conditions for PPV's and P3AT's almost inevitably create defects, alternating donor-acceptor conjugated polymers are conventionally prepared via Suzuki and Stille cross-coupling reactions,[18–25] which in theory yield a perfectly alternating structure. These palladium catalyzed cross-coupling reactions combine a dihalogenated (mostly dibrominated) (hetero)aryl monomer with either a bistannylated (Stille) or a boronic acid/ester bifunctionalized (hetero)aryl (Suzuki) monomer. However, a few recent reports reveal that the catalytic cycle does not always proceed as projected, resulting in the formation of unexpected monomer combinations and hence deviations of the projected (simplified) chemical structure (**Figure 2**).[26–29] These studies also show a pronounced (negative) effect on the final solar cell performance. As such, it is clear that additional efforts should be made to properly analyze the structural purity of alternating donor-acceptor copolymers.

Besides structural imperfections of the conjugated backbone, it has also been shown that the end groups of the donor-acceptor polymer chains can lead to a substantial variation of the final device performance. Bazan and coworkers for instance observed a substantial increase in efficiency for polymer solar cells prepared from poly[(4,4-didodecyldithieno[3,2-*b*:2',3'-*d*]silole)-2,6-diyl-*alt*-(2,1,3-benzothiadiazole)-4,7-diyl] (PDTSBT; **Figure 3**), from 4.2 to 4.7%, when the bromide and stannyl functional groups at the end of the polymer chains were replaced by thiophene units.[30] Since this seminal report, end-capping has become a rather common part of the standard polymerization procedure for donor-acceptor copolymers. However, in most cases, one merely assumes that the polymer is end-capped and a detailed analysis of the end groups is missing, although this information would be very relevant. End-group analysis can in fact be very enlightening, since it can reveal information about the occurrence of side reactions, which generally limit the molar mass. The absence of these data can mainly be attributed to the difficulty to analyze conjugated push-pull polymer end groups by standard characterization techniques.

In this progress report, we aim to increase the awareness that the real chemical structure of push-pull copolymers can substantially differ from the projected one. It is shown that homocoupling can be a prevalent side reaction, which can seriously affect the properties and (device) performance of the final materials, even when present in (very) low amounts. Therefore, the importance of thorough analysis of the polymer structure is addressed. Furthermore, it is shown that knowledge of the end groups can be very helpful to gain insight in the reaction mechanism, which can then be used to further optimize the reaction conditions and improve the material quality.

2. Homocoupling

Metal-catalyzed cross-coupling reactions have become a very powerful tool for the creation of carbon-carbon bonds. The term ‘cross-coupling’ refers to the fact that an aryl (or vinyl) halide is coupled with an organometallic nucleophile. However, besides the desired cross-coupling, coupling of two identical aryl halides or two organometallic nucleophiles can occur as well. This is generally referred to as ‘homocoupling’.[31–35] In standard organic syntheses, these side reactions are often neglected, since the generated small amount of impurities can easily be removed. However, these side products cannot be ignored when such cross-coupling reactions are applied to prepare polymers, as they induce non-removable structural defects. Although it is well known from standard organic chemistry work that these side reactions do occur, very limited reports have evaluated (or even mention) the occurrence of homocoupling in push-pull type conjugated polymers and their effect on the material and device properties, and in particular reproducibility, is probably underestimated.

2.1. Literature observations – the effect of homocoupling on solar cell performance

One of the first indications of polymer backbone structural impurities in alternating donor-acceptor copolymers prepared via Suzuki polymerization was provided by R. Janssen and coworkers.[26] They were intrigued by the fact that the UV-Vis absorption profile of similar

DPP-based polymers (prepared by different research groups) showed different features, i.e. slight changes of the onset values and the appearance of shoulders. It was reasoned that the deviation of the UV-Vis spectra should be caused by a modification of the conjugated polymer backbone. Via deliberate introduction of a homocoupled DPP monomer in PDPPTPT (Figure 3), they were able to mimic the deviation of the UV-Vis spectra, which made them suggest that this type of defects was present in many DPP-based polymers. Almost half of the 131 DPP-based articles they assessed showed a deviation of the UV-Vis spectrum, which can possibly be related to homocoupling.[26] Furthermore, it was shown that these homocoupling defects can be created during the polymerization process when suboptimal reaction conditions (ratio Pd/ligand) are used and that a small amount (5%) of these defects can already have detrimental effects on solar cell performance. The authors emphasized that homocoupling defects can lead to low-lying energy trap sites and that they can effectively increase the HOMO (highest occupied molecular orbital) and decrease the LUMO (lowest unoccupied molecular orbital) energy levels of the polymers, leading to a decreased photocurrent and a significantly lower solar cell performance, with a power conversion efficiency (PCE) dropping from 7.5 to 4.5% (although in this particular example the molar mass difference has to be taken into account as well).

One year later, similar observations were made by the group of Luping Yu.[27] They noticed that samples of PTB7 (Figure 3; one of the most popular push-pull copolymers at the time) with a higher polydispersity afforded lower photovoltaic performances. The red-shifted UV-Vis absorption spectra of these polymer samples encouraged them to investigate the molecular purity of the polymer backbone. To this extent, they performed of a model reaction between a monostannylated benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) and a dibrominated thieno[3,4-*b*]thiophene (TT) using the standard polymerization conditions (**Figure 4**). Identification of the different reaction products allowed to conclude that homocoupling of both the BDT and the TT monomers occurs under these conditions. In particular, homocoupling of the organotin compound was observed in quite large amounts (9%). Homocoupling can hence take place to a reasonable extent, even under ‘optimal’ reaction conditions. This suggests that the occurrence of homocoupling is difficult to predict and that subtle differences in the reaction conditions/handling (which are most likely often not considered to be different) can provoke the formation of these side reactions, diminishing the final material quality.

In 2015, our group also noticed that the photovoltaic performance of commercial PTB7 samples varied quite drastically, with PCE’s ranging from 7.0 to 2.7%.[28] It was observed (by analytical GPC measurements) that the batches with a poor photovoltaic performance consisted out of low molar mass species. Moreover, a bimodal molar mass distribution was seen. These samples also showed a more red-shifted absorption onset compared to the well-performing polymers. Because of the obvious similarity to the results reported before by Janssen et al., further initiatives were taken to investigate if homocoupling could be at the origin of these observations (vide infra).

Although UV-Vis spectroscopy can certainly be helpful to identify structural defects in the conjugated polymer backbone when different batches of a similar polymer are compared, it does not allow to pinpoint the presence of homocoupling defects in novel copolymers. For this purpose, additional analysis techniques have to be employed. Most often, the chemical structure of this type of copolymers is analyzed by NMR spectroscopy. However, this is usually not straightforward and special attention is required to record NMR spectra with satisfactory signal-to-noise ratio and to correctly interpret the spectra. Because of slow rotation and effective π-π stacking of the push-pull conjugated polymer chains, broad signals in the ^{1}H NMR spectra are regularly observed, impeding straightforward analysis. Recording the NMR spectra at elevated temperatures (e.g. 120 °C) can improve the quality of the spectra, but even when narrow signals are obtained, the peaks arising from the structural imperfections are very small and identification usually requires the tedious preparation of model compounds. Hence, it is clear that elucidation of the correct chemical structure by NMR spectroscopy can be quite laborious for most push-pull copolymers, discouraging most synthetic polymer chemists. Therefore, alternative analysis techniques have to be implemented.

In our group, we have been using MALDI-TOF mass spectrometry to identify the presence of homocoupled species. This was illustrated first in our study on commercial batches of PTB7.[28] MALDI-TOF analysis was performed in an attempt to find direct proof for the occurrence of homocoupling sequences. From these measurements it was clear that the conjugated backbone of all low molar mass commercial samples contained homocoupled units, originating from both the electrophilic (bromoaryl) TT and nucleophilic (organotin) BDT monomer (**Figure 5**). The presence of these defects resulted in a lower polymer bandgap and an upward shift of the HOMO energy level, resulting in a decreased open-circuit voltage (V_{OC}) for the resulting polymer solar cells. Moreover, these homocoupling defects also appeared to diminish the hole mobility of the polymers, increase the number of trap states and alter the final film morphology. However, one has to keep in mind that similar effects are also caused by a reduction in molar mass and the two effects (i.e. homocoupling and molar mass) are not easily disentangled.

Although MALDI-TOF allows to qualitatively identify homocoupled species in the molecular backbone of conjugated polymers, it is not possible to quantify the amount of homocoupling by mass spectrometry. In this respect, studies on small molecule reference systems can be very insightful. ^{1}H NMR analysis of small molecules usually does not suffer from signal broadening and, due to their low molar mass (< 5000 g/mol) and increased solubility, they can be analyzed with a variety of analytical techniques. The number of reports on the influence of homocoupling on the performance of small molecules in organic electronic applications is, however, even more limited than for polymers. This can mainly be attributed to the purification steps which can be conducted much more efficiently on small molecules.

Homocoupled impurities are often readily removed by conventional silica column chromatography. As such, their initial presence in the crude reaction mixture is probably often overlooked.

In 2016, we observed the presence of homocoupling impurities in a small molecule material.[36] The initial goal of our study was to vary the central donor unit of the well-known DTS(FBTTh$_2$)$_2$ electron donor molecule (**Figure 6**) and to investigate its effect on the physicochemical and device properties. Although relatively low efficiencies were observed for all new donor molecules compared to the reference small molecule, one material particularly caught our attention. For this small molecule (DTP(FBTTh$_2$)$_2$, Figure 6), a remarkably low V_{OC} was observed (0.5 V), while this was not expected based on the estimation of the HOMO energy level by cyclic voltammetry. Careful analysis by both ^{1}H NMR and MALDI-TOF allowed identification of the minor impurity (less than 10% based on NMR integration) remaining in the sample as the homocoupled DTP derivative, despite the fact that the small molecule had undergone the same extensive purification procedure as the other small molecules (column chromatography and preparative recycling size exclusion chromatography (prep-SEC)). Complete removal of the homocoupled impurity, which in this case was far from trivial and could only be achieved via recycling prep-SEC, eventually increased the OPV efficiency from 1.3% to 2.8%. This increase could mainly be attributed to an improved V_{OC} and short-circuit current density (J_{SC}). It is important to note that in this case, the homocoupling impurity could not be observed by UV-Vis spectroscopy, although the absorption spectrum of the homocoupled product is significantly different. As such, small amounts of homocoupling are – also in the case of polymers – likely not identifiable by UV-Vis and the absorption spectrum is not sufficient as a proof for a defect or defect-free structure.

Small molecule systems also allow to more systematically investigate the effect of homocoupling on the device properties, since both the target small molecule and the homocoupled small molecule can be prepared independently in a very pure state and then mixed in a specified ratio. To this extent, we synthesized the homocoupled analogue of DTS(FBTTh$_2$)$_2$ (Figure 6) and mixed this with the pure compound in specific ratios (0, 10, 20, 50 and 100%).[37] Again, it appeared very difficult to identify the presence of small quantities of homocoupling impurities by UV-Vis spectroscopy, since only very small deviations of the absorption onset were observed for the lowest concentrations of homocoupling. Nevertheless, such low quantities (5%) are sufficient to substantially decrease the solar cell performance. Especially for the V_{OC}, a clear trend could be observed in function of the presence of the homocoupled species. Increasing the concentration of the homocoupled side product lead to an almost exponential decrease of the V_{OC}. This V_{OC} drop is in agreement with the observations made in previous reports and seems typical for the presence of homocoupled nucleophilic (electron-rich) monomers.

2.2. The origin of homocoupling

From the previous section it is clear that homocoupling can occur both in Stille and Suzuki cross-coupling reactions. Because of the strong similarity between both, only the homocoupling pathways for the Stille reaction will be discussed here.

In scientific literature, the Stille process is generally represented by a simple catalytic cycle comprised of three subsequent steps: i) oxidative addition, ii) transmetalation and iii) reductive elimination (**Figure 7**, top). From this picture, it appears that the Stille reaction proceeds very selectively, without notable side reactions. However, in reality, the mechanism of the Stille reaction is much more complex. To illustrate the complexity of the Stille process, P. Espinet used a nice metaphor. In his 2015 review on the Stille reaction, the catalytic cycle was compared with a subway map.[23] The simplified, most commonly used representation can then be compared with the metro of Sevilla, which has only one line, almost eliminating the possibilities to make mistakes. However, the true Stille reaction resembles the subway map of New York or Moscow and, to make things even more complicated, you are making the trip with blind eyes. Figure 7 (bottom) also shows a more detailed catalytic cycle. Although this is still a simplification, it can be seen at a glance that much more pathways are available than expected based on the commonly used catalytic cycle. Furthermore, it is also important to mention that some of the reactions are reversible, which easily gives rise to unwanted side products, especially when the irreversible reductive elimination step is slow.

Several reports have already shown that homocoupling of both the organometallic nucleophile and the aryl halide can occur and several mechanisms toward the formation of these side products have been postulated (**Figure 8**).[20,38,39] Homocoupling of the organostannane proceeds via reaction with a Pd(II) catalyst. These oxidized Pd species can be reduced back to Pd(0) by a double transmetallation step with the aryltin species, which is then followed by a reductive elimination step to yield a homocoupled biaryl species. Therefore, application of Pd(II) salts as catalysts (e.g. $Pd(PPh_3)_2Cl_2$) inevitably introduces homocoupled side products. Furthermore, Pd(II) moieties can also be formed during the reaction via the presence of oxidizing species converting Pd(0) to Pd(II). One of the most evident oxidizing impurities is molecular oxygen. For this reason, synthetic chemists try to conduct the Stille cross-coupling very carefully under nitrogen or argon atmosphere to avoid the presence of oxidizing impurities. However, even when the reaction is hypothetically conducted free of oxidizing impurities, homocoupling can still be observed. The origin of this effect can be found in one of the homocoupling pathways of the arylhalogen species. After the oxidative addition step, the Ar-Pd(II)-Br species can undergo an aryl-group exchange with another Pd-aryl species instead of undergoing transmetallation with the aryltin species.[40–43] A disproportionation step will then yield the homocoupled arylhalogen species, a regenerated Pd(0) entity and a Pd(II) species. This generation of the Pd(II) species then opens up the above-described homocoupling pathway of the aryltin product. Whenever the reaction is forming homocoupled arylhalogen species, this will inevitably also lead to the formation of homocoupled aryl tin species. Another possible pathway for the generation of arylhalogen homocoupling opens up when there are reducing impurities in the reaction mixture. These agents will reduce Ar-Pd(II)-Br complexes to Ar-Pd(0)$^-$, which is followed by oxidative addition of another arylhalogen species. The Ar-Pd(II)-Ar complex will then undergo reductive elimination, forming the homocoupled Ar-Ar species and regenerating Pd(0).[44]

Despite these basic mechanistic insights, very limited efforts have been done to optimize Suzuki and/or Stille polymerizations to minimize the occurrence of homocoupling defects. In their report on homocoupling in PDPPTPT polymers, R. Janssen et al. also investigated the correlation between homocoupling and the palladium-to-ligand ratio ($Pd_2(dba)_3$:PPh_3).[26] PDPPTPT synthesized with a suboptimal 1:1 palladium:ligand ratio had a lower molar mass (M_n = 47 kDa) as compared to all other polymers synthesized with an ‘ideal’ 1:2 catalyst system (M_n above 72 kDa). A possible reasoning provided is that the reaction suffers from an imbalance in monomer feed ratio due to homocoupling side reactions (or degradation of the catalyst).

In 2016, M. Sommer and co-workers found that the palladium precursor has a substantial influence on the extent to which homocoupling occurs in PCDTBT polymers (Figure 3) synthesized via Suzuki polycondensation.[29] By careful analysis of the ^{1}H NMR spectra of different polymer batches they could identify homocoupling of the carbazole monomer as an important side reaction (**Figure 9**). $Pd(PPh_3)_4$ was the only catalyst which afforded homocoupling-free PCDTBT via Suzuki polycondensation. Other catalytic systems ($Pd_2(dba)_3$/phosphine, third generation Buchwald catalyst G3/phosphine and G2/P(*o*-tol)$_3$) all gave homocoupling of the carbazole unit, ranging from 2 to 8%, leading to a strong reduction of the OPV device performance (PCE = 3.5%) compared to virtually homocoupling-free polymers (PCE = 7%). A similar investigation for a Stille polycondensation was done by Y. Li et al. for the synthesis of PDQT (Figure 3).[45] The following three catalytic systems were used: $Pd(PPh_3)_2Cl_2$, $Pd_2(dba)_3$/P(*o*-tol)$_3$ (with a molar ratio of 1:4) and $Pd(PPh_3)_4$. Similarly, it was found that $Pd(PPh_3)_4$ generated polymers with the fewest defects, although in this case not homocoupling-free. The worst performing catalytic system appeared to be $Pd(PPh_3)_2Cl_2$.

From the available literature, it appears that some monomers might be more prone to homocoupling than others, which should then have an electronic origin. However, at this point, it is impossible to postulate general relationships between the monomer structure and reaction conditions leading to (the absence of) homocoupling due to the very limited amount of studies in this direction so far. Therefore, careful analysis of the prepared materials is highly recommended and optimization of the reaction parameters (catalyst, temperature, concentration, co-solvent, base, …) should be performed for every monomer combination to achieve the best possible materials and to avoid batch-to-batch variations.

3. End groups of push-pull type conjugated polymers

Besides structural imperfections in the conjugated backbone, the functional groups remaining at the end of the polymer chains can also influence the final material and device properties. Therefore, profound analysis of the end group functionalities should also be part of the standard chemical analysis of conjugated polymers. Moreover, the end groups can also provide mechanistic insights on the polymerization process and explain why certain polymer batches do not reach high molar masses.

For metal-catalyzed cross-coupling polycondensations employed to prepare push-pull copolymers, it is often assumed that the halogen and organometallic functional groups are still present at the end of the polymer chains after the reaction. However, for this type of reactions it is known from research on small organic molecules that different side reactions can occur, such as protodeborylation,[46–48] dehalogenation,[49–51] ligand exchange[52–56] and hydroxylation,[57,58] which terminate the growing polymer chains. Although identification of the end groups can hence be very insightful, only very limited efforts have been devoted to studies that go beyond the mere preparation of the desired materials. Some of the most noteworthy structural analysis studies were performed for Suzuki polycondensations. Polymers prepared by Suzuki reactions tend to show lower molar masses as compared to copolymers prepared by Stille, one of the reasons the field nowadays mostly uses Stille. For most donor-acceptor combinations, the Suzuki conditions need to be fully optimized to increase the molar mass of the resulting polymer. In this respect, end group analysis is very perceptive.

A pioneering study in this field was performed by R. Janssen and coworkers in 2001.[49] To widen the scope of Suzuki polycondensations, the reaction conditions were optimized and bis(pinacolato)boronic ester precursor monomers were employed to allow the successful polymerization of 2,5-thiophenebisboronic derivatives. In-depth analysis of the chemical structure and end groups was performed via MALDI-TOF. It was shown that the main side reaction hindering the formation of high molar mass polymer chains, irrespective of the catalyst ($Pd(OAc)_2$ or $Pd(PPh_3)_4$), was hydrolytic deborylation.[46–48] By using $Pd(PPh_3)_4$, the number of different end groups and hence the number of chain types could significantly be reduced, pointing to inhibition of several undesired reaction pathways. Nevertheless, the use of $Pd(PPh_3)_4$ did introduce a reasonably large amount of aryl-aryl exchange between the triphenylphosphine ligands and the Pd center in $Ar\text{-}Pd\text{-}[(PPh_3)_2]\text{-}X$, impeding the formation of high molar mass polymers. Somewhat surprisingly, the introduction of branching in the side chain of the diiodobenzene monomer effectively suppressed this side reaction, allowing the formation of high molar mass polymer.

Another noteworthy study was reported by J. Sakamoto and coworkers.[58] In an attempt to prepare poly(*m*-phenylene) via Suzuki polycondensation under conventional conditions using $Pd(PPh_3)_4$ as a catalyst, they observed only oligomeric products. Through analysis of the chemical structure of the polymer/oligomeric materials, the authors could identify several side reactions (**Figure 10**). None of the chains contained a bromide or organoboron end group, which indicates that termination reactions occurred. Moreover, also cyclic derivatives were formed. Careful analysis of the MALDI-TOF spectra allowed to identify the different end groups, originating from ligand scrambling,[52–56] protodeborylation[46–48] and hydroxylation[57,58] (Figure 10). Although the MALDI-TOF spectra provided evidence that all of these side reactions were occurring, ligand scrambling appeared to be the main side reaction limiting the formation of high molar mass species. This termination reaction could be suppressed when the more sterically hindered ligand SPhos was used. Furthermore, slow addition of the monomer limited the formation of cyclic polymers, allowing the polymer chains to grow to high molar masses and a more uniform chemical structure of the different chains (Figure 10).

Although MALDI-TOF is a very suitable technique to get a quick impression of the end groups of a push-pull conjugated polymer, it also has some drawbacks. The most important limitation of MALDI-TOF analysis is the fact that this technique is most sensitive for polymers with rather low molar masses. MALDI-TOF spectra for conjugated polymers with molar masses exceeding 15 kDa are rarely found. Additionally, MALDI-TOF analysis does not allow straightforward quantification, complicating elucidation of the dominant side reaction. In this respect, NMR analysis can be very complementary. M. Sommer et al. employed NMR to determine the end groups of PCDTBT-based low bandgap polymers.[50] By comparison of the ^{1}H NMR spectra of the synthesized polymers with those of the monomers and specifically designed model compounds, they were able to identify dehalogenation as the major side reaction hindering the polymerization.[49–51] However, NMR spectroscopy has its limitations as well. Especially for high molar mass polymer chains, the signals of the end groups become very small as compared to the main backbone signals and hence assignment of these signals becomes increasingly difficult. In addition, identification of the end groups often requires the preparation of model compounds. As a result, analysis of the chemical structure of conjugated polymers by NMR spectroscopy is often very laborious and therefore omitted.

Due to the similarity between the Stille and Suzuki reactions, analogous side reactions can be expected for Stille polycondensations. As mentioned before, end-capping has become an almost routine part of the Stille polymerization protocol. After the seminal report by Bazan and coworkers, indicating that the remaining bromide and/or organotin functionalities can adversely affect the OPV device performance, it has become a common practice to add a mono-functionalized aryl compound to the reaction mixture to end-cap the polymer.[30,59–61] Frequently, first 2-bromothiophene is added and allowed to react with the remaining stannyl end groups of the polymer chains, followed by the addition of 2-stannylthiophene to react with the remaining bromide end groups. An extra portion of catalyst is also often added to assure that the reaction proceeds, even when the activity of the initially added catalyst diminished. An important point to consider here is the time at which the end-capping procedure is performed, as this has a major influence on the possible existence of reactive end groups. In some reports, the change in final (device) properties is used as an indirect proof for end-capping. End-capping was for instance found to avoid charge carrier traps or to eliminate the formation of undesirable chemical transformations under device operation due to remaining reactive functional groups.[30] Additionally, it can decrease the sensitivity of the active layer to layer thickness and thermal degradation. H. Wang et al. reported that end-capping of a PBTDPP polymer (Figure 3) with a porphyrin molecule enhances the light absorption in the range of 400-550 nm and thereby increases photovoltaic performance.[62] Y. Park and coworkers end-capped a series of PDTSBT polymers (Figure 3) with thiophenes and observed an enhanced intermolecular packing and a decreased device hysteresis when employed in organic field effect transistors (OFET), which was hypothesized to be induced by the removal of charge traps.[60] Thiophene end-capping increased the hole mobility by a factor of 2 to 4, depending on the molar mass of the polymer.

Although end-capping was found to alter the properties of the final materials and their resulting devices, structural analysis of the polymer chains remained very limited. In their first report, Bazan et al. employed X-ray photoelectron spectroscopy (XPS) to demonstrate the presence or absence of organotin and bromide groups in the prepared push-pull polymers. Nevertheless, XPS does not allow detailed structural analysis. In 2011, J. Hummelen and coworkers used MALDI-TOF to determine the end groups of several polymers synthesized by Stille or bis(pinacolato)diboron (BiPi) (i.e. a Suzuki-type) polycondensation.[63] For the Stille polymerization, mainly methyl end groups were detected and not the expected stannyl or bromide moieties. These methyl end groups originate from methyl transfer from the tin center to the polymer. Transfer of the sp^2-carbon of the stannyl compound to the catalytic complex normally proceeds much faster than sp^3-carbon transfer. As such, it is often considered unlikely that the methyl groups undergo transmetallation to the catalytic Ar-Pd(II)-Br species. Nevertheless, the observations made by Hummelen et al. demonstrate that this can still be an important side reaction during the Stille polycondensation.

In our group, we have also been using MALDI-TOF for end-group analysis of donor-acceptor copolymers, showing that multiple end groups can be present after the polymerization. It was observed that some polymers gave a rather clean MALDI-TOF spectrum, with only a limited amount of different polymer chain distributions. As an example, the MALDI-TOF spectrum of PCPDTQx$_{ff}$ is shown in **Figure 11** (left). Although the polymer was end-capped with thiophene, only two different end groups could be observed (methyl and hydrogen) and no polymer chains bearing thiophene end groups were detected. This supports the previous findings by Hummelen et al. For this particular polymer, it was observed that almost all terminal quinoxaline moieties contained methyl end groups. The distribution of polymer chains and end groups can also be much more complex, as illustrated by the example of the push-pull polymer PDTPalkTTTBAI (Figure 11, right), showing multiple different end groups (even unknown ones).[64] The fact that bromide end groups can still be observed for some polymers, while they are absent for others, indicates that the occurrence of side (termination) reactions can be dependent on the nature of the different monomers and the employed reaction conditions. Structural analysis of the polymer chains is hence very worthwhile to prevail and understand the origin of low molar masses and poor material properties. Furthermore, it can also be very helpful to optimize the polymerization reactions by avoiding side reactions to occur. Ligand exchange reactions, which appear to be major side reactions in the Suzuki polycondensation, seem to be almost absent in the Stille polycondensations. However, since organotin functional groups are more labile then organoboron moieties, it is difficult to state whether destannylation occurs during the polymerization, the workup of the reaction or upon MALDI-TOF analysis.

4. Direct (hetero)arylation

So far, only Suzuki and Stille polycondensation reactions have been discussed here. However, during recent years, another cross-coupling method has gained a lot of attention for the preparation of push-pull organic semiconductors, i.e. direct (hetero)arylation polymerization (DArP). The reaction mechanism of DArP is related to those of other cross-coupling procedures. However, these polymerizations do not require organometallic precursors – certainly advantageous in terms of atom economy, (toxic) waste (in case of Stille) and 'synthetic complexity' of the final materials – but use a (hetero)aryl monomer with activated C-H bonds instead.[65–68] Therefore, it is commonly believed that DArP will become increasingly important in the field of conjugated polymers. However, as most monomers contain multiple C-H bonds, the direct arylation reaction can proceed at various positions, introducing structural impurities (i.e. branches) in the polymer backbone. As a consequence, in this field, a lot of work has already been performed to reveal the true chemical structure of the resulting polymers and to fully optimize the reaction conditions to allow the preparation of defect-free materials. Mostly, ^{1}H NMR spectroscopy has been used to investigate the chemical structures of the different polymers, which is again far from trivial and requires the synthesis of dedicated model compounds to assign chemical shifts.[50,69,70] Despite its laborious character, careful ^{1}H NMR analysis has caused a remarkable progress in this field during the last few years. In the early days of DArP, most studies just reported the synthesis of a conjugated material, while thorough (device) characterization of the prepared materials was often missing, probably due to their poor quality. By careful chemical analysis of the prepared materials and optimization of the reaction conditions several side reactions could be monitored and eliminated, finally leading to the preparation of conjugated materials with comparable (or even better) properties than the materials prepared via classical Stille or Suzuki reactions.[71–73] Detailed analysis of the chemical structure combined with a large variation of the reaction conditions has also led to a fast learning track with regard to the influence of several reaction parameters on the occurrence of side reactions. A more detailed overview of this work is considered out of the scope of the present progress report and we refer the interested reader to recent papers and reviews on DArP.[65–73]

5. Conclusions

To date, most state of the art push-pull type copolymers are prepared by Stille or Suzuki polycondensation reactions. Often, minimal attention is paid to the chemical analysis of the polymers, since a perfectly alternating structure is expected due to the nature of these reactions. However, several recent reports have shown that side reactions do occur during the polymerizations and, in contrast to small molecule synthesis, these side products are incorporated in the polymer chains and cannot simply be removed by common purification procedures. An important side reaction is homocoupling. For applications in organic photovoltaics, it has been seen that homocoupling defects in the conjugated backbone severely influence the final device performance. Especially the V_{OC} appears to be very sensitive to small amounts of homocoupling defects. Therefore, it can be reasoned that not only the molar mass is responsible for the commonly observed batch-to-batch variations, but also the possible presence of homocoupling plays an important role. To our opinion, careful analysis of the chemical structure of push-pull copolymers should hence become a standard procedure. In some cases, UV-Vis spectroscopy can be a first and easy tool to compare different polymer batches, but MALDI-TOF mass spectrometry and NMR spectroscopy are clearly more instructive. The application of MALDI-TOF to the analysis of (push-pull) conjugated polymers has been rather limited so far, probably in part due to the fact that it is considered to be ‘challenging’ to get a decent spectrum for high molar mass polymers. However, the use of electron transfer matrices such as *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) has greatly improved the sensitivity for the analysis of conjugated polymers.[74]

Insight in the end group distribution can also be of great interest. Currently, synthetic chemists regularly incorporate an end-capping procedure in their synthesis protocols to remove remaining bromide and organometallic groups. However, detailed analysis of the end groups has shown that several side reactions (e.g. ligand exchange, methyl transfer, …) compete with the desired cross-coupling reaction and terminate the polymerization. Knowledge of the end groups can be very helpful to optimize the reaction conditions and gain a better understanding of the most crucial reaction parameters. It should be noted that, in this respect, the community working on DArP is the better pupil of the class. Analysis of the chemical structure has received much more attention in this field, leading to a significant progress over the past few years. It should be mentioned as well that the results discussed here are mainly situated in the field of organic photovoltaics. It can, however, be expected that these effects generate similar issues in other device applications (e.g. OPDs, OFETs, …). The results are hence relevant for the wider organic electronics community.

Acknowledgements

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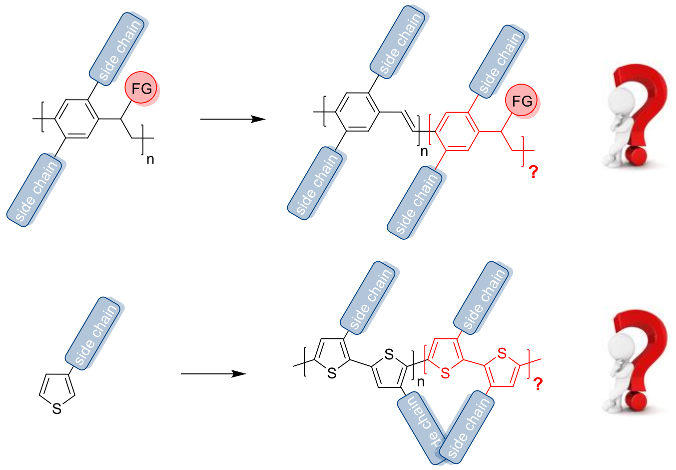


Figure 1. Top: Illustration of structural defects in PPV-based conjugated polymers due to incomplete elimination. Bottom: Illustration of structural defects in P3AT-based conjugated polymers due to undesired head-to-head coupling.

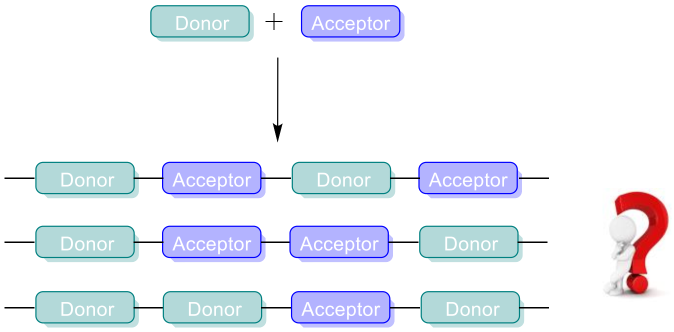


Figure 2. Formation of homocoupling defects in push-pull type copolymers, breaking the alternation of donor and acceptor building blocks.

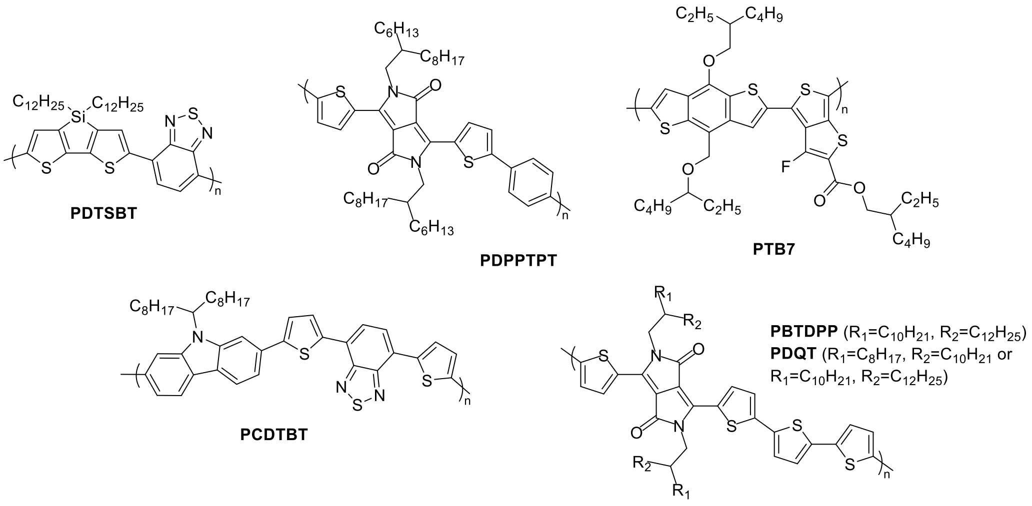


Figure 3. Structures of the low bandgap copolymers discussed in this report.

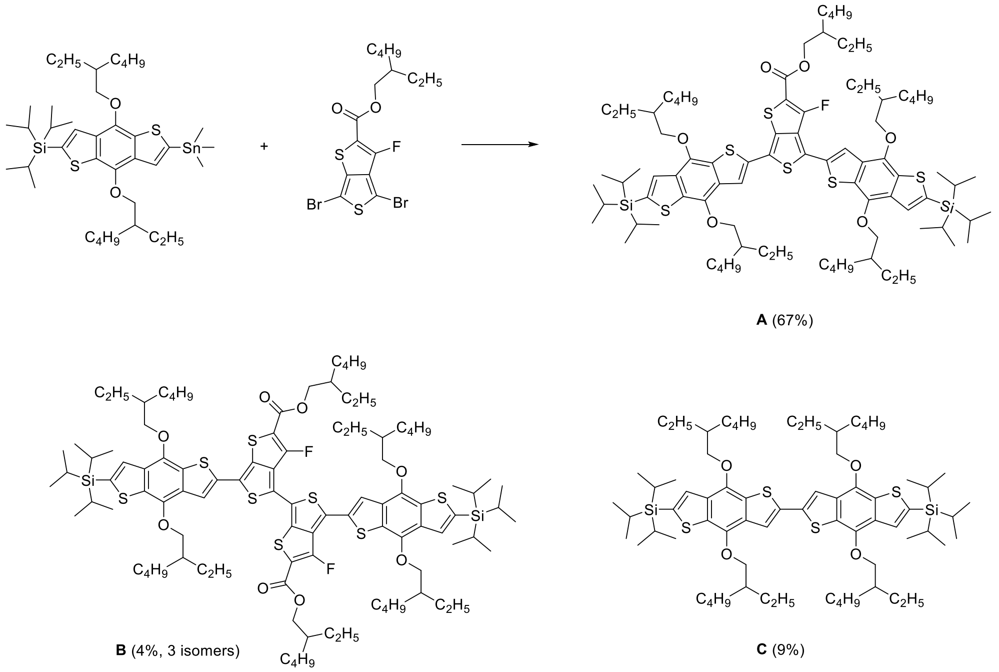


Figure 4. Model reaction between mono-stannylated BDT and dibrominated TT under the standard polymerization conditions for PTB7.[27] (Reproduced with permission. Copyright © 2015, American Chemical Society.)

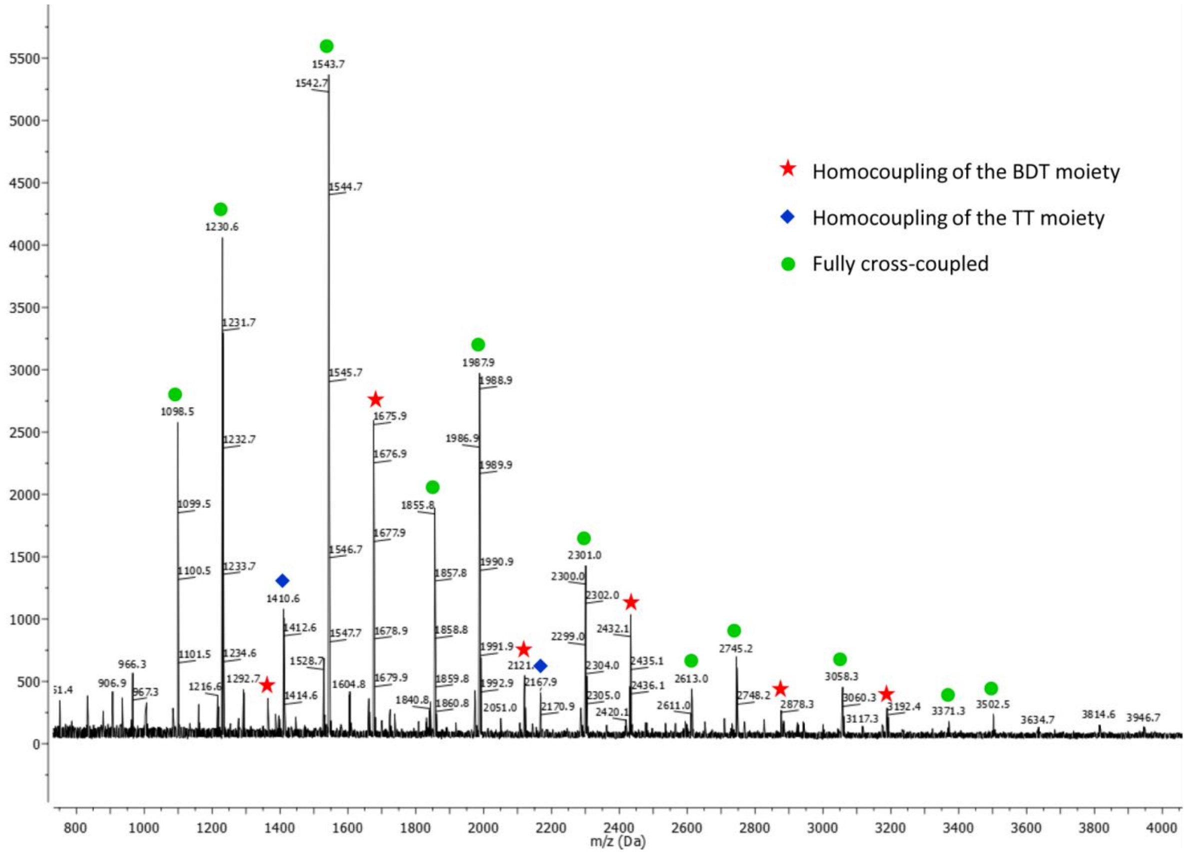
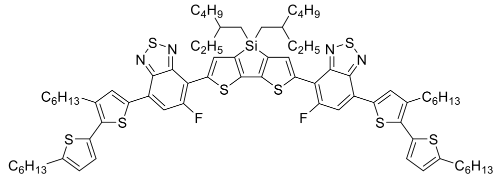
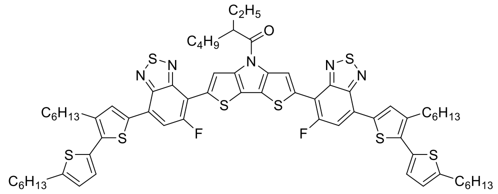


Figure 5. MALDI-TOF mass spectrum of low molar mass PTB7, showing the presence of homocoupled species along the polymer chains.[28] (Reproduced with permission. Copyright © 2015, American Chemical Society.)



DTS(FBTTh$_2$)$_2$



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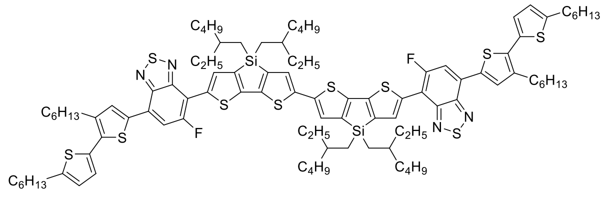

DTS$_2$(FBTTh$_2$)$_2$

Figure 6. Structures of small molecule analogues DTS(FBTTh$_2$)$_2$, DTP(FBTTh$_2$)$_2$ and DTS$_2$(FBTTh$_2$)$_2$.

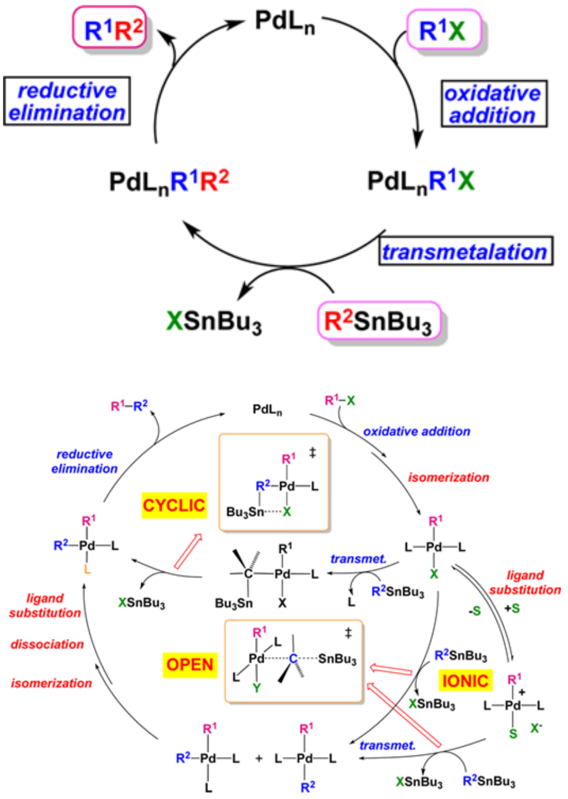

Figure 7. Top: Simplified catalytic cycle of the palladium-catalyzed Stille cross-coupling as shown in most scientific literature. Bottom: A more detailed Stille cycle.[23] (Reproduced with permission. Copyright © 2015, American Chemical Society.)

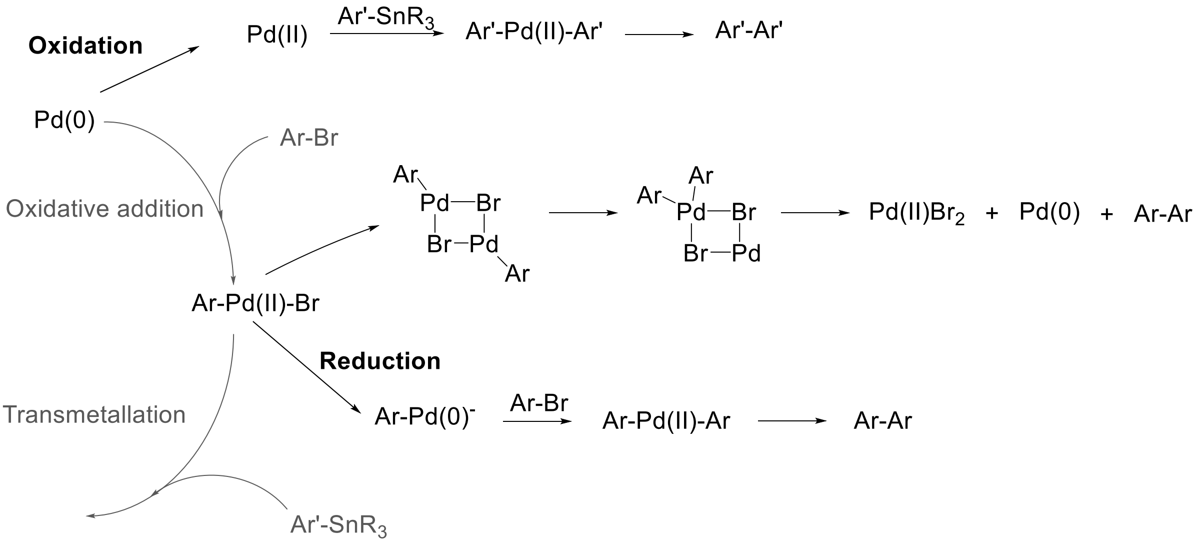

Figure 8. Homocoupling pathways for the Stille cross-coupling.[38] (Reproduced with permission. Copyright © 2015, John Wiley and Sons.)

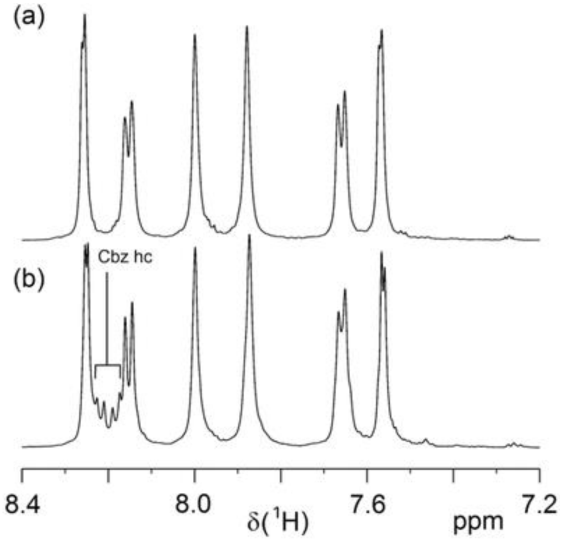

Figure 9. ^{1}H NMR spectra of PCDTBT with 0 and 10 mol% carbazole homocoupling (Cbz hc) (in a and b, respectively) in $C_2D_2Cl_4$ at 120 °C.[29] (Reproduced with permission. Copyright © 2016, John Wiley and Sons.)

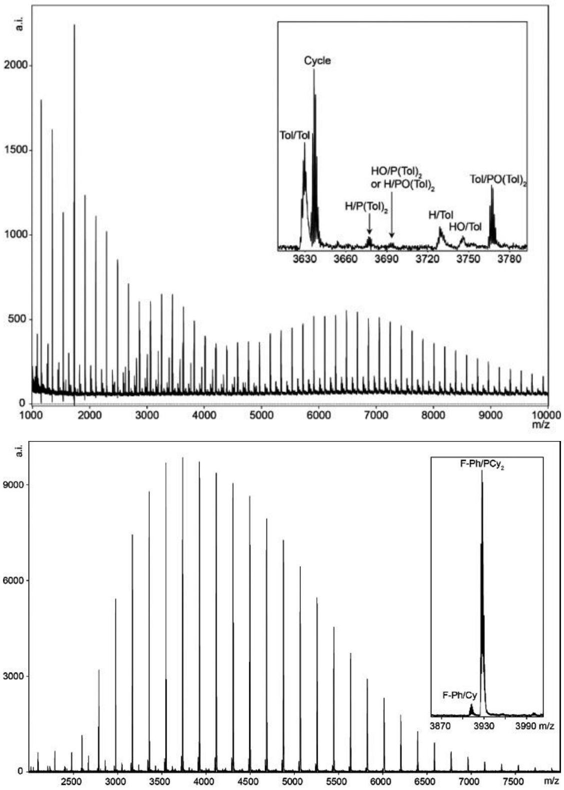

Figure 10. MALDI-TOF mass spectrum of poly(*m*-phenylene) synthesized via Suzuki polycondensation with either only $Pd(PPh_3)_4$ as the catalyst (top) or with the addition of the sterically hindered ligand SPhos (bottom). X/Y (X, Y = H, OH, Tol, $P(Tol)_2$ or $PO(Tol)_2$) represents the end-group situation of the obtained polymer species.[58] (Reproduced with permission. Copyright © 2012, American Chemical Society.)

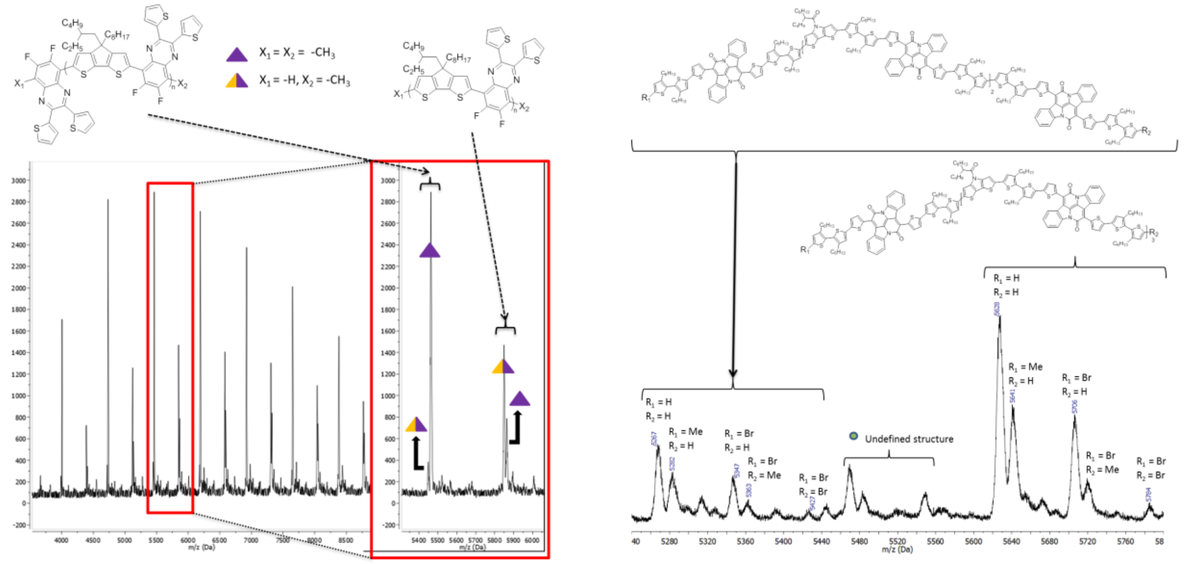

Figure 11. MALDI-TOF mass spectra of $\text{PCPDTQx}_{\text{ff}}$ (left) and PDTPalkTTTBAI (right).[64]

Wouter Maes obtained his PhD in Chemistry at the KU Leuven in 2005 under the supervision of Prof. W. Dehaen. After that he has been working as a postdoctoral fellow of the FWO Vlaanderen in the same group, focusing on porphyrinoid materials. External postdoctoral stays were conducted in Paris (Prof. E. Rose) and Oxford (Prof. H. Anderson). In November 2009, he was appointed Assistant Professor at Hasselt University. At present, he is Associate Professor and heading a research group focusing on the synthesis of novel small molecule and conjugated polymer materials for organic electronics and advanced healthcare.

Table of contents entry

The structure of push-pull type conjugated polymers – very popular nowadays in the field of organic electronics – is often not as simple as projected. Structural imperfections in the polymer backbone (for example homocouplings) and different end groups may occur, which have a significant influence on the final device performance.

Donor-acceptor conjugated polymers

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On the ‘True’ Structure of Push-Pull Type Low Bandgap Polymers for Organic Electronics