FOCUS REVIEW

Synergistic catalysis for the synthesis of semiconducting polymers

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Abstract

Organic semiconductors have received much interest over the past few decades. As the field has progressed, so has the complexity of the molecular structures of organic semiconductors. Often, the highest-performing organic semiconductors (i.e., those with the highest charge mobility or those that provide the highest power conversion efficiencies in organic photovoltaics) involve complex syntheses, making them very challenging to synthesize, even by experienced synthetic chemists. In this focused review, we report on recent efforts in developing more efficient synthetic pathways. Specifically, the concept of synergistic catalysis, which involves the use of two or more catalysts with orthogonal reactivity to enable reactions that are not possible with the use of a single catalyst, is introduced. Synergistic catalysis allows for controlled polymerizations, room-temperature reactions, and/or polymerizations with greater regioselectivity, opening the door to more time-, labor-, cost-, and energy-saving methods for synthesizing semiconducting polymers.
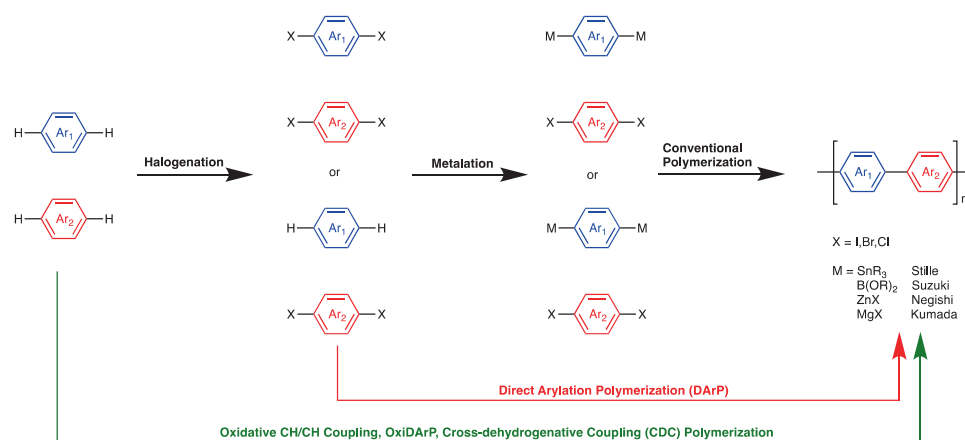
Introduction

Over the past few decades, a tremendous amount of research has been performed in the area of organic semiconducting polymers regarding their potential applications in organic light-emitting diodes [1–3], organic photovoltaics [4–6], organic field effect transistors [7–9], photodetectors [10, 11], sensors [12, 13], and more recently in bioelectronics [14, 15]. It is appealing to use them in such applications because the resulting devices can be made to be lightweight and flexible; moreover, the devices can be fabricated in a cost-effective manner using solution processing, and the resulting materials are highly tunable, allowing for the design of materials with varied bandgaps, charge mobility, ionic conductivity, and biocompatibility. The research into the above organic electronics devices has been enabled by the development of organic semiconducting polymers with increasing complexity, which has also resulted in an increase in the environmental burdens and rising costs of polymer synthesis [16, 17].

Organic semiconducting polymers are typically synthesized using metal-catalyzed cross-coupling reactions, including Stille, Suzuki, Kumada, or Negishi cross-coupling reactions (Scheme 1 – black arrow) [18–20]. While these reactions enable powerful transformations, they require prefunctionalization (e.g., halogenation followed by metalation) of the monomers, thereby introducing additional steps in the overall synthesis. Furthermore, the reactions require the use of stoichiometric amounts of an organometallic species. Direct arylation polymerizations (DArP) (Scheme 1 – red arrow), and more recently, oxidative CH/CH coupling, also known as OxiDArP or cross-dehydrogenative coupling (CDC) polymerizations (Scheme 1 – green arrow), have been the focus of much interest for overcoming the issues related to more conventional metal-catalyzed cross-coupling reactions. Unfortunately, these reactions also suffer from regioselectivity issues that can lead to branching and cross-linking, and homocoupling introduces defects into the polymer backbone. Another complication is that living polymerizations have been challenging to achieve using DArP and CDC polymerizations.

To address the challenges related to achieving selectivity and control over polymerization reactions, our group has been exploring the use of two catalysts to obtain reactivities that were not previously attainable. Synergistic catalysis involves the use of at least two different catalysts to activate two different substrates to allow for previously unattainable transformations (Scheme 2) [21, 22]. Despite the advantages
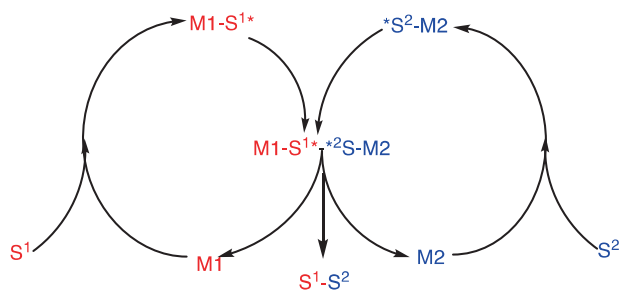
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Scheme 1 Routes to the synthesis of alternating semiconducting polymers. The conventional route is shown with black arrows, where the halogenation and metalation of precursors are required to generate monomers for polymerization. The red arrow depicts direct arylation

polymerization (DArP) where halogenation of one of the monomers is needed. Finally, the green arrow depicts oxidative CH/CH coupling or cross-dehydrogenative coupling (CDC) polymerization where no prefunctionalization is needed
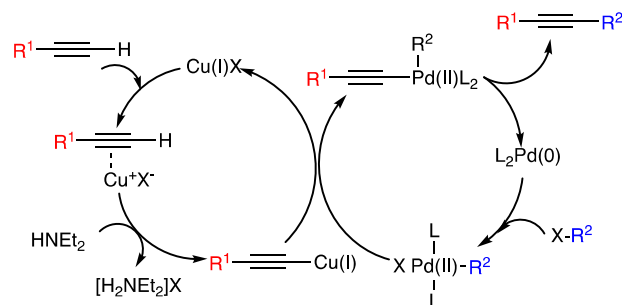

Scheme 2 Scheme represents the essence of synergistic catalysis. Transition metal catalyst M1 activates only S^1; transition metal catalyst M2 activates only S^2. This allows for a reaction to occur between S^1 and S^2 that would be unattainable if only one of the substrates was activated

Scheme 3 Sonogashira cross-coupling reactions of alkynes and aryl iodides

that synergistic catalysis can offer, its examples remain limited because it can be difficult for a catalyst to selectively activate one substrate over another, and monocatalytic side reactions must be avoided. Synergistic catalysis has been reviewed for small-molecule reactions [21, 22]. This paper will focus on the use of synergistic catalysis, specifically dual transition metal synergistic catalysis, for semiconducting polymer synthesis with some attention to what our group has recently achieved in this area.

Bimetallic systems

Pd/Cu Sonogashira

The archetypical reaction of dual transition synergistic catalysis is the Sonogashira reaction, which involves the alkynylation of aryl iodides using Pd(0)/Cu(I) dual catalytic conditions (Scheme 3). While different modes of reactivity have been reported, traditionally, it is believed that the

reaction begins with the oxidative addition of Pd(0) into the halide to form a Pd(II) complex. Simultaneous activation of the alkyne occurs through the coordination of Cu(I). Transmetalation between the two activated substrates leads to the regeneration of Cu(I) as well as the formation of Pd(II) acetylide. The regeneration of Pd(0) is achieved through reductive elimination, which also yields the cross-coupled product. The use of Pd(0)/Cu(I) dual catalysis allows the reaction to occur under milder conditions (i.e., at room temperature), whereas the monometallic versions either involve the use of a stoichiometric amount of metal (in the case of Cu) or high temperatures (with catalytic Pd).
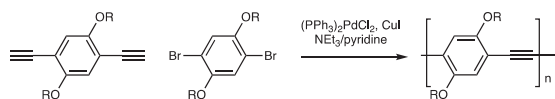
This concept has been applied in semiconducting polymer synthesis to the synthesis of poly(phenyleneethynylene)s (PPEs) [23], which, as the name implies, consist of alternating phenyl and alkynyl units. The first example of a successful synthesis of soluble PPE derivatives was reported in 1990 by Giesa and Schulz (Scheme 4) [24]. A Sonogashira reaction between a dibrominated monomer and bisalkynyl monomer yielded polymers with a moderate degree of polymerization (DP) with cross-linking. The use of a dibrominated monomer necessitated the use of high temperatures for polymerization,

which is thought to be the origin of the cross-linking. To circumvent these issues, Wrighton [25] and Weder [26] used diiodinated monomers, which allowed for polymerizations to occur at room temperature or below 70 °C. Similarly, soluble PPE derivatives with DPs as high as 230 were obtained by Swager using this strategy [27], and the authors used end-capping or an excess of one monomer to reduce the DP.

Pd/Cu modified stille cross-coupling

Traditional Stille cross-coupling involves a single transition metal catalyst (usually Pd(0)) and is a reaction between halides and stoichiometric equivalents of organostannanes. Pd/Cu dual catalytic versions of Stille coupling have also been reported to enhance the reaction compared to the single-catalyst reaction, allowing room temperature conditions to be used. In the traditional mechanism, the reaction is commonly believed to occur via oxidative addition, followed by the transmetalation of the organostannane with the Pd(II) complex, with C-C bond formation occurring through reductive elimination (Scheme 5a), regenerating Pd(0). For the Pd/Cu dual catalytic version (Scheme 5b) [28, 29], the proposed mechanism is thought to proceed through the transmetalation of the organostannane with the copper catalyst. The Pd catalytic cycle is similar to that of the traditional mechanism such that the transmetalation of the organostannane is replaced by the transmetalation of Cu(I). This step regenerates Cu(I) for the Cu catalytic cycle.

While many semiconducting polymer syntheses have relied on using traditional Stille cross-coupling, there is one example where modified Stille coupling was used [30, 31]. This was done to allow for a controlled polymerization to synthesize PPE. Catalyst transfer polymerizations (CTPs) have been successfully developed to allow for the
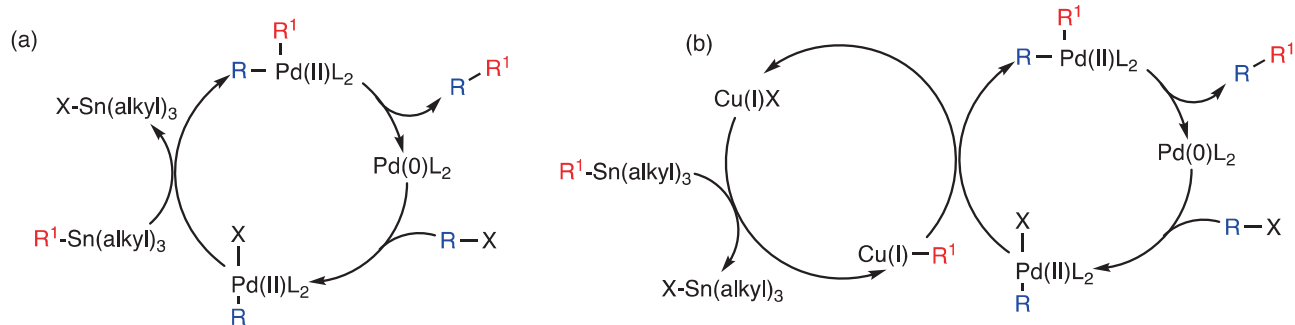
controlled synthesis of conjugated polymers, including polythiophenes, polyfluorenes, and polyphenylenes [32]. Most methods rely on using the Kumada and Suzuki cross-coupling reactions. Regardless of the stoichiometric organometallic reagent used, control over the polymerization is thought to be achieved through the formation of a π-aryl complex between the Ni or Pd catalyst (Scheme 6a). To achieve a controlled polymerization for the synthesis of PPE, Bielawski et al. found that the traditional Stille cross-coupling conditions using a single Pd catalyst were insufficient to achieve chain polymerization and that catalytic amounts of CuI, as well as additional ligands, were required to afford living polymerization (Scheme 6b) [30]. To provide experimental support of the polymerization displaying living characteristics, the authors showed that the polymers could chain extend by the addition of an extra batch of monomer. Surface-initiated polymerization was also performed to support that the mechanism for polymer growth is chain polymerization.
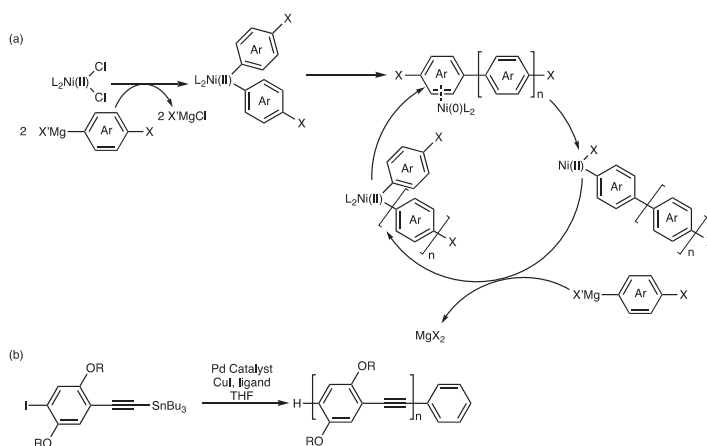
Au/Pd systems

Our own foray into dual transition metal catalysis began through a desire to develop a living DArP for the synthesis of π-conjugated polymers. Up until this point, our own work had focused on using Kumada catalyst transfer polymerization (KCTP) (Scheme 6) to achieve living polymerization [33–39]. In the case of the synthesis of poly(3-hexylthiophene) (P3HT), KCTP proceeds through the in situ generation of 2-bromo-3-hexyl-thienylmagnesium halide, which is then polymerized by a Ni catalyst. The commonly accepted mechanism for KCTP is the initiation of the polymerization through transmetalation, which generates Ni(0), followed by a cycle that consists of oxidative addition, transmetalation, and reductive elimination. As mentioned above, upon reductive elimination, Ni(0) is believed to coordinate with the conjugated π-system, preventing chain transfer through intermolecular catalyst transfer. While KCTP is highly effective, it does suffer from

Scheme 4 Synthesis of dialkoxy-PPE [24]

Scheme 5 a Traditional Stille cross-coupling; **b** Pd/Cu dual transition metal catalyst-assisted Stille cross-coupling

Scheme 6 a KCTP mechanism highlighting the importance of the Ni(0)-π-aryl complex between the Ni or Pd catalyst; **b** Synthetic scheme to achieve CTP using a modified Stille coupling

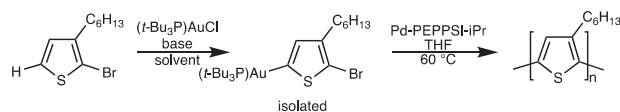Scheme 7 CTP involving an organogold monomer and Pd catalyst

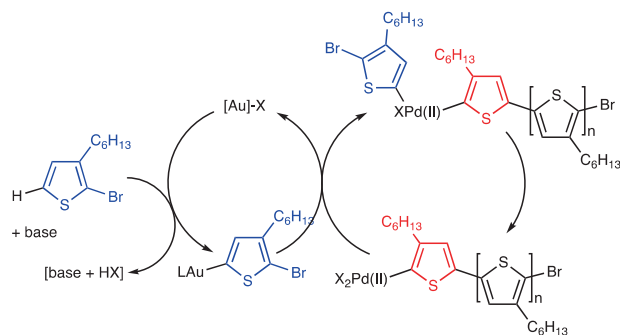the need to use a stoichiometric amount of organomagnesium and a bishalogenated precursor.

To overcome these issues, in 2011, Mori et al. reported a method for synthesizing P3HT using a monohalogenated thiophene precursor where the Grignard monomer was synthesized through deprotonation [40]. Subsequently, reports of using DArP followed where a single transition metal catalyst was used, thereby bypassing Grignard formation [41–43]. Unfortunately, these DArP methods lack control over molecular weight and dispersity. We hypothesized that a dual metal catalytic method, where two different metals with orthogonal reactivity are used, could facilitate first the activation of a C-H bond and then a controlled polymerization.

Our initial attempts to achieve such a reaction focused on the use of Au as the metal to facilitate C-H bond activation because of its reported ability to activate C-H bonds in electron-deficient (hetero)aromatic units and its ability to undergo transmetalation with Pd(II) and Ni(II)—this latter feature was particularly attractive because Pd and Ni have both enabled controlled CTP for synthesizing semiconducting polymers. Au/Pd transmetalation has been shown to be effective in small molecule-modified Sonogashira cross-coupling reactions, the carbometallation of alkynes, and modified Stille reactions [44–46]. Given this propensity for Au/Pd transmetalation to occur, we reasoned that if a Au(I)-thiophene monomer could be accessed, a polymerization should proceed upon the addition of Pd.

Studies began by using reported conditions to synthesize the Au-thiophene complex [47]. Specifically, 2-bromo-3-hexylthiophene was reacted with chloro(tri-*tert*-butylphosphine)gold(I) in the presence of base to obtain the desired product (Scheme 7). Polymerization of the organogold monomer was achieved by the addition of a Pd catalyst [48]. Catalyst screening was performed to elucidate the best Pd source, and it was ultimately found that Pd-PEPPSI-iPr facilitated a polymerization that showed living characteristics whereby chain extension occurred upon the addition
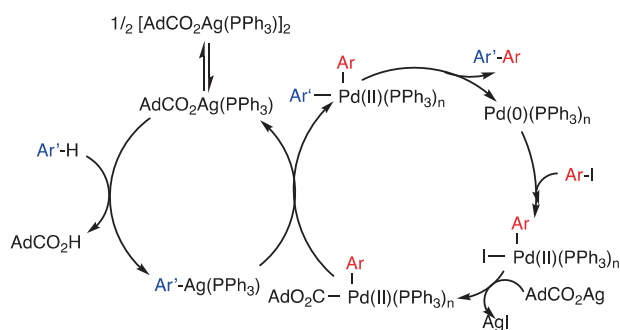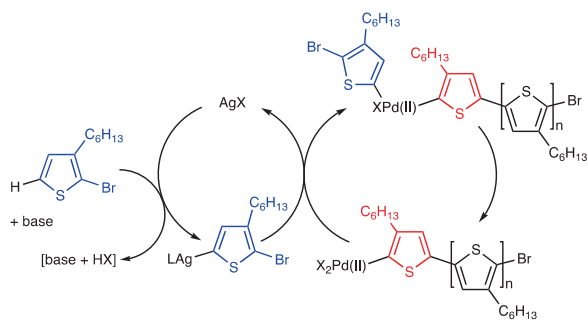

Scheme 8 Ideal mechanism for an Au/Pd-mediated CTP

of extra monomer after the initial monomer had been consumed. The polymerization also showed a linear relationship with the number-average molecular weight (M_n) and monomer conversion, suggestive of controlled polymerization. The dispersity ($Đ$) ranged from 1 to 1.3.

While these initial findings of Au/Pd transmetalation occurring to promote P3HT synthesis were exciting, polymerization was only possible with the isolated Au-thiophene monomer. When the Au-thiophene monomer was generated in situ, the polymerization did not proceed upon the addition of a Pd catalyst. The transmetalation step is driven by the formation of a Au(I)-X bond (Scheme 8) [49]. If X is a halogen, the bond is sufficiently strong to push the reaction forward. The synthesis of the Au-thiophene monomer requires a stoichiometric amount of base to remove the proton. A stoichiometric amount of base means that an alkoxide or hydroxide is coordinated to Pd; thus, the formation of a Au(I)-OR bond needs to drive transmetalation, but the Au(I)-OR bond is not sufficiently strong to do so. While Au/Pd dual catalytic Sonogashira and

Scheme 9 Cross-coupling reaction enabled by Ag(I)-mediated C-H activation
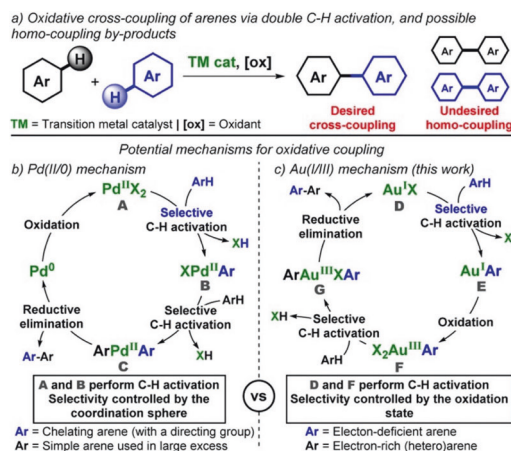

Scheme 10 Proposed Ag/Pd dual catalytic synthesis of P3HT

Stille couplings can occur in the absence of a base, C-H activation requires the presence of a base. Ultimately, we were not able to achieve a Au/Pd dual-metal catalytic system for polymerizations.

Pd/Ag systems

DArP

While we were struggling with Au/Pd-mediated DArP, reports started to emerge on the topic of Ag/Pd-mediated small molecule direct arylation reactions (Scheme 9) [50, 51]. Ag(I)-salts are added frequently to Pd-catalyzed C-H functionalization reactions, but they are often presumed to act as halide scavengers or oxidants in the case of oxidative functionalization. However, studies performed independently by Larrosa [50] and Sanford [51] showed that Ag(I)-carboxylates are able to carry out C-H activation on arenes. These studies encouraged us to move away from Au/Pd-mediated DArP toward Ag/Pd-mediated DArP (Scheme 10) [52]. Initially, the conditions of our attempts led to broad molecular weight distributions. We hypothesized that this occurred because of the ability of Pd to activate the C-H bond along with Ag, resulting in the nonorthogonal reactivities of the two metals. To obtain orthogonal reactivity, pyridine was added to the reaction. PEPPSI-iPr contains 3-chloropyridine, which acts as a stabilizing ligand. It has been reported that religating Pd with
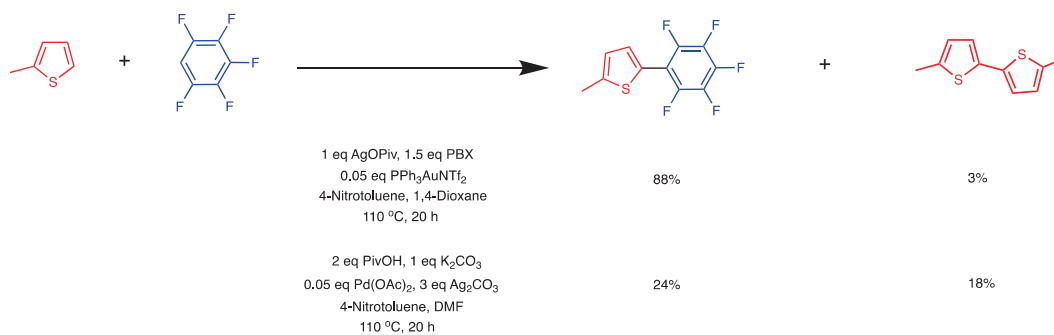

Scheme 11 a General scheme showing the desired cross-coupled product in a CDC reaction. Proposed mechanisms for CDC using **b** Pd and **c** Au. Reproduced with permission from the American Chemical Society [65]

pyridine allows it to play an inhibitory role in the catalytic process [53]. We thus hypothesized that the addition of pyridine would inhibit Pd from playing an active role in C-H activation. While we did not perform kinetic studies to verify that this did indeed take place, we nevertheless found that the addition of pyridine led to a narrower molecular weight distribution. Through this, we were able to achieve the first, and thus far only, reported case of DArP showing chain polymerization characteristics [54]. The addition of an extra equivalent of monomer after the consumption of the monomer led to chain extension, which also suggested living characteristics for the polymerization.
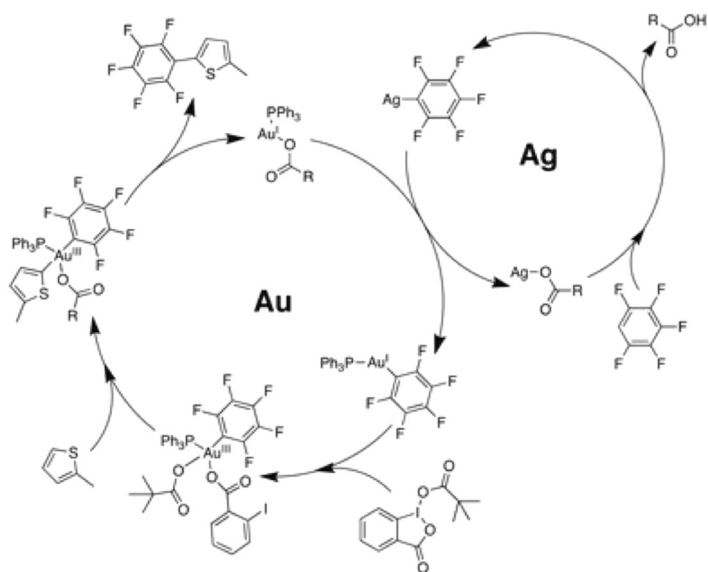
CDC polymerizations

As mentioned in the introduction, CDC polymerizations are very attractive from the point of view of achieving a more efficient synthesis of conjugated polymers. However, selectivity, specifically obtaining cross-coupling without any homocoupling, remains challenging. In our initial foray into CDC polymerizations, we began by going through the small molecule literature to identify effective small molecule CDC reactions (Scheme 11a) that could be transferred over to polymerizations. Specifically, we identified Pd-based (Scheme 11b) and Au(I)/Au(III)-based (Scheme 11c) CDC reactions as possible starting points [55]. It is worth noting that when we initially started our literature search, the understanding of these reactions is not what it is now, and the mechanisms shown below we now know are not applicable when attempting polymerization. Nevertheless, since the reported small molecule Pd CDC reactions typically required a large excess of one of the coupling partners to afford high yields, we initially decided to focus on Au(I)/Au(III) reactions. At the onset, Au(I)/Au(III)-based reactions seemed more suitable due to their cross-selectivity

Scheme 12 Small-molecule model reactions for Au-based and Pd-based CDC polymerizations

Scheme 13 Proposed CDC mechanism that involves Ag- and Au(III)-mediated C-H activation. Reproduced with permission from the Royal of Society Chemistry [56]
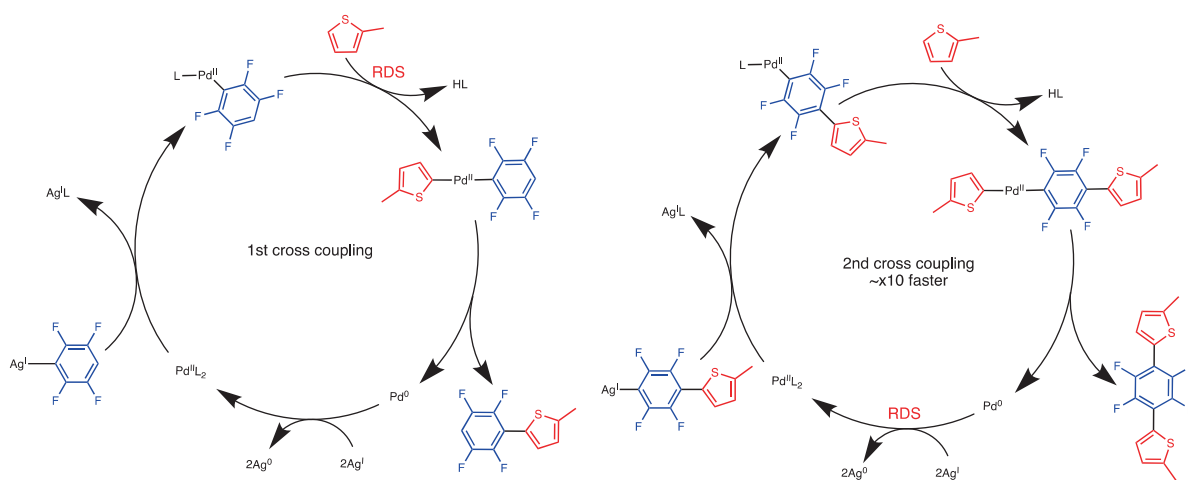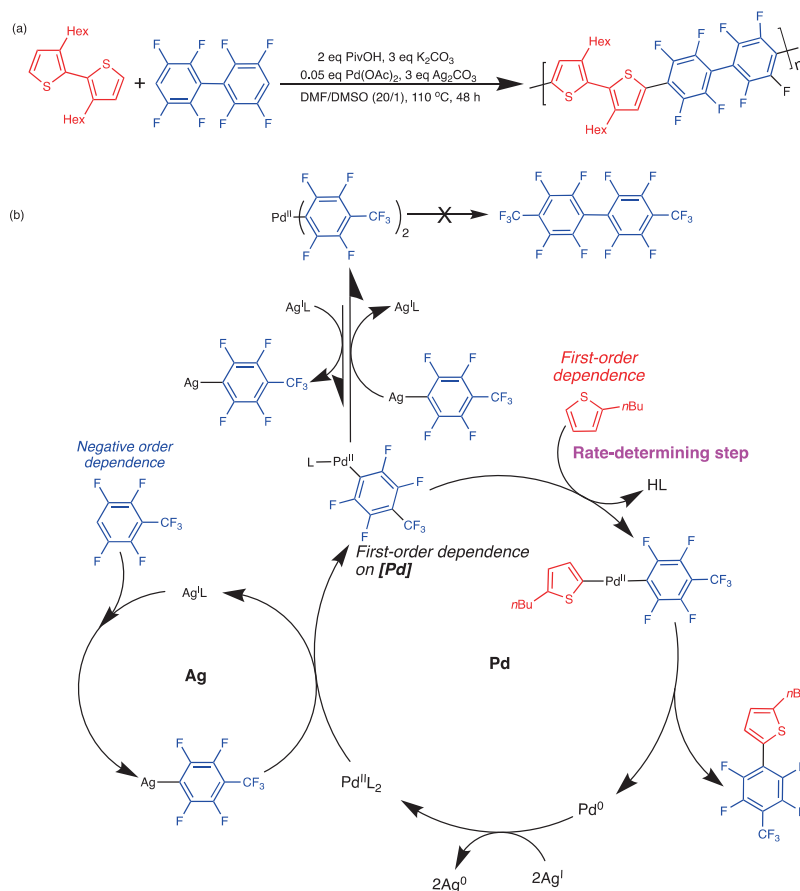

based on the electron density of the monomers, making it appealing for the synthesis of donor-acceptor (D-A) polymers. Additionally, the ability to run the reaction with high yield while using stoichiometric ratios of the two molecules to be cross-coupled would be preferred for polycondensations where the Carothers equation is obeyed. Indeed, our initial small molecule studies supported that the Au(I)/Au(III)-based reaction would be more suitable for transferring to polymerization because of the high yield and low degree of homocoupling observed (Scheme 12) [56, 57].

Unfortunately, despite optimization reactions being attempted, we were never able to obtain polymers with sufficiently high M_n (<10 kg mol^{-1}) [56]. Additionally, a large amount of homocoupling was observed, with the % alternation remaining limited to 67–76%, where 100% alternation indicates no homocoupling. This surprising result and reports that started to emerge at the time of Ag participation in C-H activation led us to investigate the mechanism further, and we discovered that instead of a Au(I)/Au(III)-based system, the reaction involved Ag-mediated C-H activation, and instead of the electron-

deficient monomer being activated by Au(I), it was activated by Ag. Ag-mediated C-H activation is followed by transmetalation to Au(I), which becomes oxidized to Au(III), at which point Au(III) also activates the electron-rich species. Reductive elimination then leads to the cross-coupled product (Scheme 13). This mechanism was later also presented by Zhu [58] and Hong [59]. In particular, Hong et al. showed through density functional theory that the chemoselectivity of the reaction was driven by the acidity of the electron-deficient species and nucleophilicity of the electron-rich species. Once a cross-coupled dimer is formed, both the acidity and nucleophilicity decrease, leading to increasingly lower chemoselectivity and reactivity as the polymer grows.

At around the same time, we were performing these studies, Kanbara et al. published a highly effective CDC polymerization using Pd (Scheme 14a) [60]. They later showed that this polymerization was also Ag-mediated, altering the originally proposed mechanism (Scheme 14b) [61]. We were very intrigued as to why this reaction worked as well as it did, given the poor performance observed in
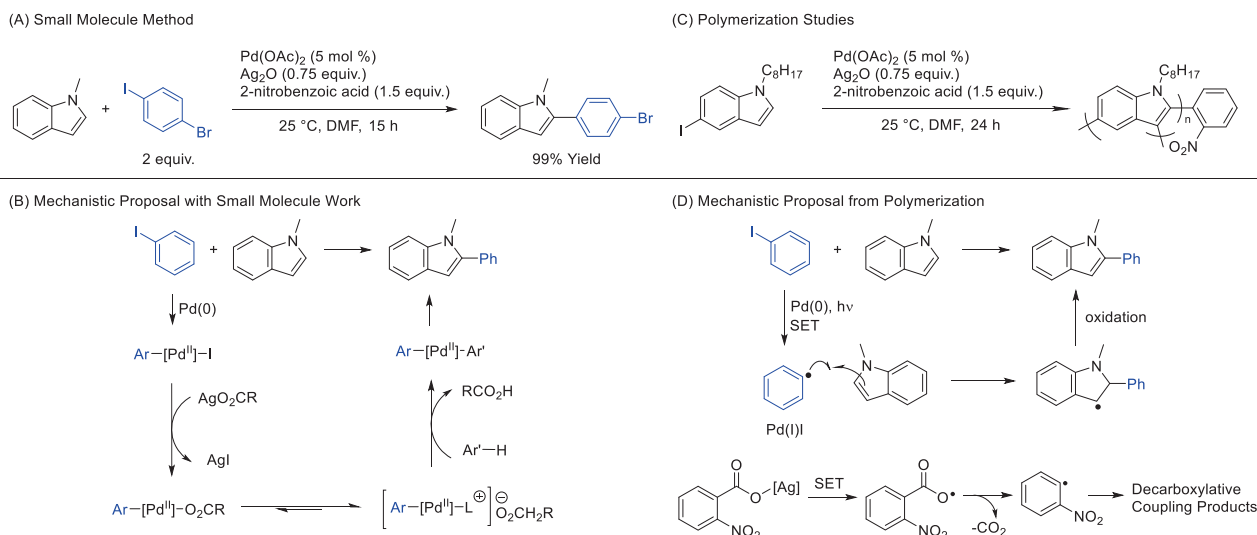
Scheme 14 a Pd/Ag-mediated CDC polymerization and **b** its proposed mechanism
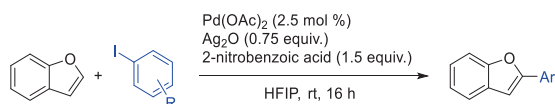

Scheme 15 Proposed mechanism of Pd/Ag-mediated CDC. In the 1st cross-coupling reaction, the rate-determining step (RDS) is the C-H activation of thiophene. In the 2nd cross-coupling reaction, the C-H activation is much faster, rendering the oxidation of Pd by Ag as the RDS

our small molecule model studies and the seemingly similar mechanism between the Ag/Au-cocatalyzed system vs. the Ag/Pd-cocatalyzed system. In both cases, Ag activates the electron-deficient species with Au or Pd activates the electron-rich species, and the stark difference in performance was surprising. We began by looking at the reaction between a cross-coupled dimer and a monomer to produce a cross-coupled trimer. In the Ag/Au-cocatalyzed system, the cross-coupled dimer showed significantly reduced reactivity compared to the monomer. However, in the Ag/Pd-cocatalyzed system, the cross-coupled dimer showed greater reactivity than the monomer [57].

Scheme 16 **a** Small-molecule room-temperature direct arylation of indole and **b** the originally proposed mechanism. **c** DArP of indole and **d** newly proposed direct arylation mechanism. Reproduced with permission from the American Chemical Society [66]

Scheme 17 Room-temperature benzofuran direct arylation by aryl iodide using hexafluoroisopropanol (HFIP) as the solvent. Reproduced with permission from the American Chemical Society [64]

With this in mind, our group performed a series of kinetic studies to understand the mechanism involved in the chain extension step of the polymerization [57]. It was found that the first cross-coupling sequence to produce a cross-coupled dimer was slow and that the Pd-mediated CH activation of thiophene was the rate-determining step, as shown by Kanbara (Scheme 15). In the second cross-coupling sequence, the rate of the Pd-mediated CH activation of thiophene increased significantly, and the reoxidation of Pd(0) to Pd(II) was the rate-determining step. This change in the rate-determining step led to an unexpectedly efficient chain extension that facilitated the polymerization.

Room-temperature reactions

To make CH functionalization even more sustainable, there is a desire to move away from using high-temperature reaction conditions that are commonly used to activate a C-H bond. A handful of room-temperature small-molecule direct arylation methods have been developed. Inspired by these, corresponding polymerizations were also attempted. A notable room-temperature small-molecule direct arylation is the indole/iodoarene direct arylation reported by Larrosa [62]—the reaction proceeds in high yields at room temperature with no reported selectivity issues (Scheme 16a)—which seemed ideal to use for a polymerization.

Polymerization was attempted (Scheme 16c) but unfortunately led to low molecular weights and significant branching. Curiously, analysis of the product using MALDI-TOF showed that nitrobenzene was incorporated into the polymer, which suggested that this reaction was radical and photomediated (Scheme 16d). While the exact role of Ag is unclear at this stage, it is known that Ag is needed to facilitate the reaction and that the presence of both Pd and Ag gives rise to unprecedented room-temperature photomediated reactivity [63].

Inspired by the realization of room-temperature direct arylation, we chose to investigate whether similar hetero-aromatic structures could react in a similar manner. Indeed, it was found that benzofurans could react with iodoarenes at room temperature using similar reaction conditions as indole but replacing the solvent DMF with hexa-fluoroisopropanol (Scheme 17) [64]. Surprisingly, the reaction involving benzofuran was found not to be light-sensitive or radical-mediated and appears to be a Heck-type reaction. This reaction is also not catalytic with Ag. Nevertheless, the exploration of using a combination of Pd and Ag led us to discover a new room-temperature reaction, and we will be exploring its use in polymerizations.

Conclusions and outlook

While reports of synergistic catalysis in polymerizations remain limited, they do offer the possibility of using milder conditions to perform polymerizations and can offer ways to improve the control over different aspects of the polymerization, such as regioselectivity and molecular weight. One of the challenges in using synergistic catalysis has been

that transferring the equivalent small-molecule reactions to polymerization has not always worked. However, careful considerations of the unexpected results of polymerizations have given insight into small-molecule reactions, allowing one to elucidate a new mechanism that is operating in the reaction. As the use of synergistic catalysis in small-molecule reactions grows, so will their use in polymerizations—closer collaborations between synthetic organic chemists and polymer chemists will be important to facilitate the development of new polymerization methods.

Compliance with ethical standards

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