

## Towards Green Synthesis and Processing of Organic Solar Cells

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**Green energy**  
**Green chemistry**

**Abstract:** In 2018, several major breakthroughs have been achieved in organic solar cells (OSCs) with the record power conversion efficiency (PCE) reaching over 17%. With this increased efficiency, it is time to take a step forward to consider how to convert this technology into large scale production. For this, the economic and environmental profile of OSCs should be taken seriously – simplified synthetic routes and green chemistry methods should be applied. According to previous studies, OSCs are competitive and profitable in the commercial market. However, toxic and/or hazardous chemicals are currently used in materials synthesis and device fabrication of OSCs. In this account, we will talk about contributions and efforts we have made to minimize the economic and environmental disadvantages in the production of OSCs. We will start with the background on how our projects were conceived and will specifically discuss our work on direct arylation and green solvent. Developments of direct arylation for synthesizing conjugated polymers will be illustrated along with our recent finding regarding the effect of green solvents on device performance and stability.

## 1. Introduction

Since the first report of organic solar cells (OSCs) in 1986 by C. W. Tang,<sup>[1]</sup> significant advancements in OSCs have been achieved. To further increase the power conversion efficiency (PCE), researchers have placed enormous efforts on optimizing both material design and device structure. Earlier in 2018, a breakthrough in PCE was made by Forrest *et al.* They utilized a tandem structure solar cell with materials with complementary absorptions to maximize the collection of energy from the solar spectrum, demonstrating a PCE of 15%.<sup>[2]</sup> Recently, the PCE record has been updated to 17.27%.<sup>[3]</sup> These records have met the PCE requirement for commercialization proposed by Baker *et al.*<sup>[4]</sup> in 2009. It is now time to consider other obstacles lying in the way of the commercialization of OSCs.

In the past ten years, there have been significant changes in OSCs.<sup>[5]</sup> PCEs have increased with more complex donor materials as observed by the field moving away from the easily accessible poly(3-hexylthiophene) (P3HT) to poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b]thiophene-)-2-carboxylate-2,6-diyl] (PTB7-Th), which takes 13 steps to synthesize. Considering the fullerene derivatives' insufficient absorption profile, acceptor materials have changed from fullerene derivatives to non-fullerene compounds, which adopt a donor-acceptor structure to enhance the tunability of their absorption profiles, to harvest more energy from the solar spectrum.<sup>[6]</sup> Tandem devices of convoluted structure are also

often applied to target a champion PCE.<sup>[2,3]</sup> However, the PCE threshold for commercialization estimated by Baker *et al.* in 2009 was based on carbon-60 (C<sub>60</sub>), copper and tin phthalocyanines (CuPc and SnPc) with the structure of a single junction solar cell,<sup>[4]</sup> which may not be suitable to evaluate modern OSCs. Expenses have multiplied with the complication of chemical synthesis and device fabrication techniques currently used to obtain a high PCE. These elevated expenses in turn increase the requisite PCE threshold, because more energy needs to be generated to offset the increased manufacturing cost within a limited device lifetime. We need to update the evaluation system for the economic profile of OSCs and explore other competitive options towards industrialization, besides improving PCE. Moreover, considering future large scale production, efforts should be taken to minimize or eliminate any detrimental effects on our environment.

## 2. Economic and Environmental Profile

Light absorbing layers in OSCs are usually 100 – 200 nm, three orders of magnitude thinner than silicon based solar cells. With roll-to-roll printing, we can maximize material utilization, thus minimizing waste, making the overall cost of OSCs competitive with silicon solar cells. Additionally, using roll-to-roll printing requires significantly less stringent processing conditions. Rather than requiring high vacuum processing techniques, roll-to-roll printing only requires an inert atmosphere. Plus, roll-to-roll printing is a continuous processing technique – imagine printing solar cells in the way that newspapers are printed. These excellent advantages regarding cost and productivity assure the market viability of OSCs.

There have been a number of papers investigating roll-to-roll printing techniques for industrial production of OSCs, and satisfactory results have achieved.<sup>[7]</sup> In the beginning, to achieve a flexible device and allow sunlight to penetrate in, indium tin oxide (ITO) sputtered PET films were applied as substrates. The rest of the functional layers, such as zinc oxide, the light absorbing layer, poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS) and silver electrode, were deposited onto the substrate in sequence by printing.

To study the economic profile of OSCs in a quantitative manner, the concept of energy payback time (EPBT) has been introduced. The EPBT of a power generating system is the time required to generate as much energy as is consumed during production and lifetime operation of the system. In 2010, Krebs *et al.* reported an ambient roll-to-roll printing process called Process One.<sup>[8]</sup> Encapsulated solar cells based on the structure of PET/ITO/ZnO/P3HT:PCBM/PEDOT:PSS/Ag achieved moderate PCEs of 2-3%, with an EPBT ranged from 1.35 to 2.02 years. Two years later, the same group further reduced the EPBT to 86 days by a new method called Process H.<sup>[9]</sup> They replaced the expensive ITO front electrode with solution processable graphene and selected more cost-effective PEDOT:PSS solution and silver ink for hole transporting layer and back electrode. In addition to the expense reduction, the devices by Process H showed no reduced PCE. More recently, a paper by Krebs *et al.* reported a fabrication method for roll-to-roll printed ITO-free

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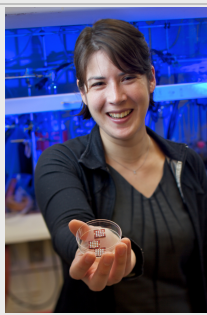
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OSCs, utilizing Ag grid and PEDOT:PSS as the front electrode to further lower the manufacturing cost; however, the stability of these encapsulated devices is still being studied. By the time the paper was published in 2017, these devices showed less than 20% degradation of PCE after 4 years of indoor storage. The lifetime of 7-8 years could be possibly achieved if the same progress continues.<sup>[10]</sup> Considering this reasonable lifetime and relatively short EPBT, the wide application of OSCs is promising and profitable, in spite of its relatively lower PCE compared with the record of commercialized silicon solar cell, 22.8% by Sunpower.<sup>[11]</sup> As such, we may not need to match a PCE record of inorganic solar cells to achieve the commercialization of OSCs. Over past decades, we have accumulated enough experience and knowledge to overcome the fundamental challenge of PCE. We may now start to look deeper into other distinguished features that can make OSCs more competitive commercially - being lightweight, solution processable, flexible and low-cost.<sup>[12]</sup>

Yunping Huang received his B.S. and M.S. in South China University of China under the direction of Prof. Fei Huang. He is currently pursuing his PhD at the University of Washington, studying green and cost-efficient synthesis of organic semiconductors with Prof. Christine Luscombe.



Christine Luscombe received her B.A., M.A., MSci, and PhD at the University of Cambridge where she performed research under the direction of Prof. Steven Ley (for B.A. and MSci) and Prof. Andrew Holmes and Dr Wilhelm Huck (for PhD). She subsequently moved to UC Berkeley as a Lindeman Research Fellow and Trinity College Junior Research Fellow to do her post-doctoral work with Prof. Jean M. J. Fréchet. She has been at the University of Washington since 2006 and is currently the Campbell Development Professor in the Materials Science and Engineering Department.

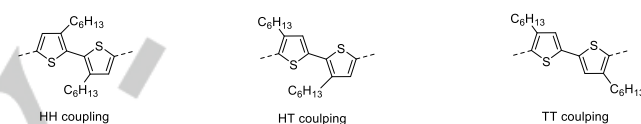


As a green energy solution, it would be ideal if the production of OSCs is green as well, minimizing its environmental impacts. However, Stille coupling is one of the most widely used synthetic methods in OSCs because of its high conversion and broad applicability. Its by-products are toxic and detrimental to the environment. In recent years, efforts have been made to eliminate the use of organotin compounds in the synthesis of organic semiconductors, and one of the most promising of these is C-H bond direct functionalization.<sup>[13]</sup> Plus, *via* the direct functionalization of C-H bond, we can also simplify the synthetic procedure by skipping pre-functionalization of monomers. This

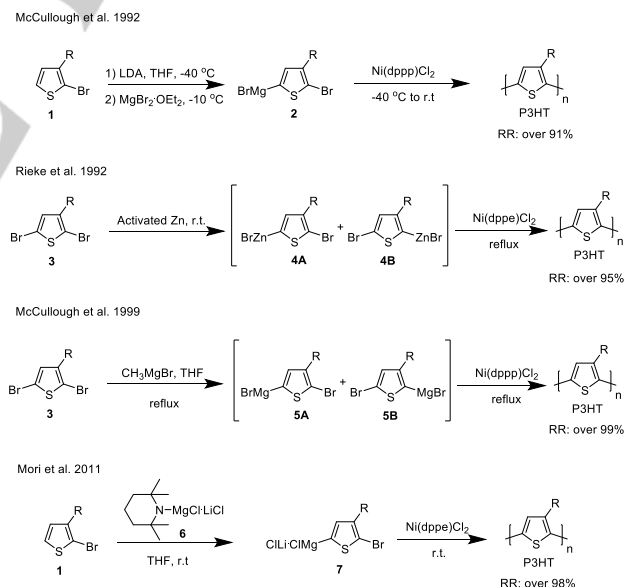
reduces the fabrication cost and waste, and boosts the production efficiency at the same time. As a member of the Center for Selective C-H Functionalization (CCHF) funded by the United States National Science Foundation, our group has been focusing on direct arylation for the synthesis of organic semiconductors. In this personal account, we share our ideas towards green and low-cost OSC products, regarding both material synthesis and device fabrication. We hope that by sharing our efforts regarding green and low-cost fabrication of OSCs, we can trigger participations and innovations to move the field forward.

### 3. Developments of Polymerization Methods for Large Scale Production

#### 3.1. Previous Methods of Regioregular P3HT Synthesis via Organometallic Reagents



**Scheme 1.** Possible orientations of monomers in P3HT.

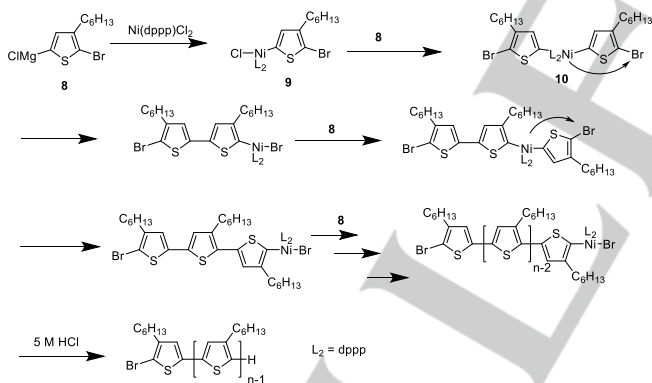


**Scheme 2.** Historic development of regioregular P3HT synthesis.

Regioregular P3HT is a commercialized conjugated polymer with a simple synthesis and excellent optoelectronic properties, showing a high potential in a wide-range of OSC applications.<sup>[14]</sup> Because of the asymmetric structure of 3-hexylthiophene, see **Scheme 1**, there are three relevant orientations when 3-hexylthiophenes are coupled with one another on the 2- and 5- positions. They are head-to-tail (HT)

coupling, head-to-head (HH) coupling, and tail-to-tail (TT) coupling, respectively. Among them, HT coupling is the most beneficial to electronics applications, because this orientation can minimize the dihedral angle between each 3-hexylthiophene moiety and their neighbors, and thus forms a more efficient conjugation along the backbone to facilitate charge transports.

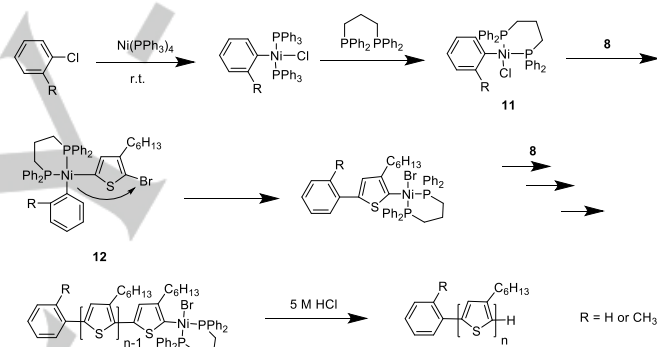
Significant efforts have been made to improve the regioregularity of the poly(3-alkylthiophene) (P3AT) family. The first synthesis of regioregular P3AT was reported by McCullough *et al.*, see **Scheme 2**.<sup>[15]</sup> It started with the selective lithiation on the 5-position of 2-bromo-3-alkylthiophene (**1**) with lithium diisopropylamide (LDA). After the addition of MgBr<sub>2</sub>, transmetalation took place and formed an organomagnesium intermediate (**2**). Polymerization began after the addition of Ni(dppp)Cl<sub>2</sub> into the system and resulting in P3AT with a regioregularity of over 90%. Later that year, Rieke *et al.* reported an alternative for the synthesis of P3AT by treating 2,5-dibromo-3-hexylthiophene (**3**) with activated zinc, followed by the addition of Ni(dppe)Cl<sub>2</sub>.<sup>[16]</sup> Activated zinc shows chemoselectivity in oxidation addition between the 2- and 5-position of 2,5-dibromo-3-alkylthiophene, giving 90% of 2-bromo-5-(bromozincio)-3-alkylthiophene (**4A**) and 10% 2-(bromozincio)-5-bromo-3-hexylthiophene (**4B**). The resulting polymer achieved a regioregularity of over 95%. When they replaced the Ni catalyst with Pd(PPh<sub>3</sub>)<sub>4</sub>, it gave a random polymer. Though these methods are encouraging for lab-scale work, both require cryogenic temperature. This is too energy intensive for large scale production, and the variation of temperature between batches may easily lead to inconsistencies in resulting products.



**Scheme 3.** Proposed mechanism of KCTP of P3HT by Yokozawa *et al.*

To overcome this, in 1999, McCullough *et al.* applied Grignard metathesis to synthesize P3HT in elevated temperature, see **Scheme 2**.<sup>[17]</sup> The treatment of 2,5-dibromo-3-hexylthiophene (**3**) with Grignard reagent resulted in two metalated isomers (**5A** and **5B**) in the ratio of 4:1, and polymerization was then triggered by the addition of Ni(dppp)Cl<sub>2</sub>. Various Grignard reagents were attempted. Most of them gave polymers with high regioregularity, and reasonable molecular weights. A more atom-efficient method was later developed by Mori *et al.* in 2011. They used (2,2,6,6-tetramethylpiperidin-1-yl)magnesium chloride·LiCl (**6**) to overcome the incomplete

halogen-metal exchange between Grignard reagents and thiophenes performed by previous studies.<sup>[18]</sup> Subsequently, polymerization were triggered by the addition of Ni(dppe)Cl<sub>2</sub> at room temperature. Polymers with high regioregularity (> 98%) and molecular weight ( $M_n = 44,900$ ) were obtained. These obtained polymers were of low dispersity, mostly ranged from 1.20 to 1.40. In 2004, McCullough *et al.* and Yokozawa *et al.* independently demonstrated that this low dispersity is ascribed to a controlled chain polymerization.<sup>[19]</sup> This polymerization is often called Kumada catalyst-transfer polymerization (KCTP), or Grignard metathesis (GRIM) polymerization, see **Scheme 3** for mechanism.<sup>[20]</sup> After Ni(dppp)Cl<sub>2</sub> is added to trigger polymerization, transmetalation to the Ni catalyst takes place, forming an intermediate, **9** and **10** in sequence. Then the intermediate undergoes reductive elimination, the C-C bond is formed and the Ni catalyst is released. Owing to the electronic rich nature of thiophene, the Ni catalyst remains closely bound to one of the adjacent thiophenes *via*  $\pi$ -d orbital interaction, resulting in the Ni-catalyst staying associated with the same chain for the duration of polymerization.



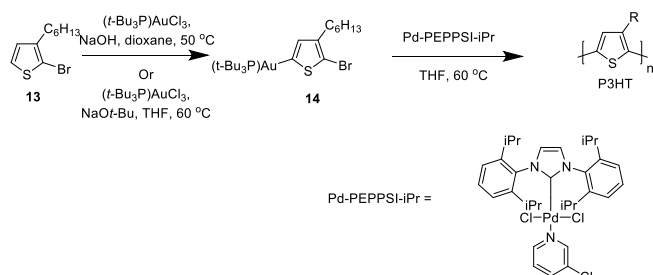
**Scheme 4.** Mechanism of externally initiated KCTP of P3HT.

To fully exploit the potentials of P3HT and enable its further functionalization towards more future applications, in 2009, our group reported a synthesis of P3HT with precise end groups and 100% regioregularity by modifying the KCTP procedure with the addition of an externally initiating Ni complex (**11**).<sup>[21]</sup> Desired end-capping groups were introduced into the Ni complexes prior to polymerization. Nucleophilic addition of Grignard reagent (**8**) to the pre-functionalized Ni complex (**11**) gives complex (**12**), which starts the growth of the polymer chain, giving a precisely end-capped fully regioregular P3HT with high molecular weight and low dispersity. We later explored simple quenching techniques after the KCTP synthesis of P3HT and successfully obtained regioregular P3HT with chalcogen end groups, either on one or both ends.<sup>[22]</sup> These end group modifications enable us to tune the compatibility between P3HT and other materials, improving the performance of organic semiconductor hybrid materials.<sup>[23]</sup>

### 3.2. New Method for Regioregular P3HT Synthesis *via* C-H Activation

The synthesis of P3HT *via* KCTP can easily provide P3HTs with excellent properties – 100% regioregularity, high molecular weight, high charge mobility, and excellent end group control. Yet,

there are still difficulties from the complex synthesis procedure, and air- and moisture-sensitive Grignard reagents are used. We believe future commercialization requires us to develop a green, safe and simplified process. Our group has been working on synthetic methods for conjugated materials that can lower the risk and expense during manufacturing, and could boost market viability and accelerate the commercialization of OSCs.

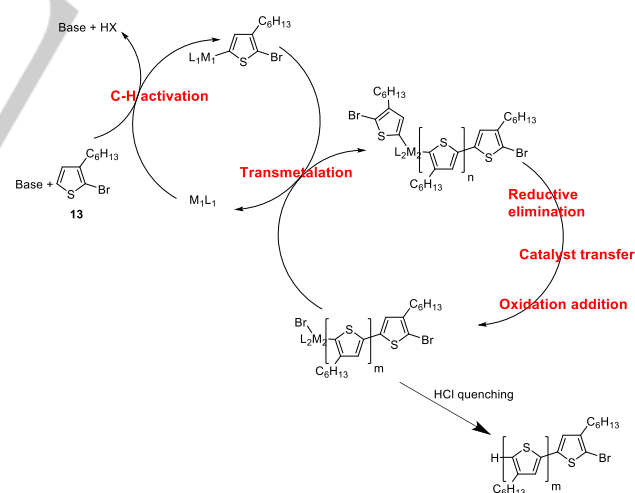


**Scheme 5.** Synthesis of P3HT *via* a gold(I) complex precursor prepared by C–H activation.

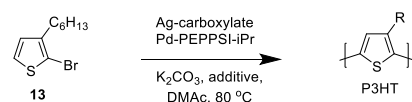
We started searching for an alternative to a Grignard reagent for pre-activating the monomer, and some attractive features of gold halides caught our attention. Studies had demonstrated that gold halides are reluctant to undergo oxidation addition into carbon-halide bonds<sup>[24]</sup> while showing an inclination to insert into electron-deficient aromatic and heteroaromatic C–H bond.<sup>[ 25 ]</sup> In addition, gold(I) compounds readily undergo transmetalation with palladium complexes.<sup>[ 26 ]</sup> In 2016, we reported the preparation of an aurylated alkylthiophene precursor *via* C–H activation for the polymerization of P3HT, as shown in **Scheme 5**.<sup>[27]</sup> The aurylated precursor (**14**) was prepared by C–H activating the 5-position of 2-bromo-3-hexylthiophene (**13**) by chloro(tri-tert-butylphosphine)gold(I) with excess base. The aurylated precursor (**14**) shows remarkable stability. Thus, we were able to isolate and purify it prior to polymerization. The subsequent polymerization was catalyzed by Pd-PEPPSI-*i*Pr, giving regioregular P3HT with degree of polymerization (DP) over 100. This result indicated the successful transmetalation between the aurylated precursor and palladium complex. Further kinetics studies demonstrated this polymerization proceeds through a controlled chain process, which explains the narrow dispersity of resulting polymers as low as 1.01.

Inspired by this result, where each transition metal reagent functions only in their separate parts in the overall process, we proposed a dual-catalytic cycle with orthogonal activity for a one-pot synthesis of P3HT with low dispersity, see **Scheme 6**. However, our previous condition with aurylation of 2-bromo-3-hexylthiophene on the 5-position required the use of stoichiometric amounts of gold, thus an alternative system for activating the 5-position was needed for a dual catalytic system. Ag-carboxylates had been shown to promote C–H activation under mild conditions,<sup>[28]</sup> and undergo transmetalation with Pd.<sup>[29]</sup> Thus we proposed an Ag–Pd dual catalyst system for this one-pot polymerization (see **Scheme 7** for reaction conditions).<sup>[ 30 ]</sup> However, because Pd is also capable of activating C–H bonds,<sup>[13]</sup>

even though Ag is dominant in this process, it resulted in the coupling of two polymer chains, demonstrating step-growth and uncontrolled polymerization. Measures to deactivate Pd toward C–H bonds needed to be taken to regain the orthogonal activity. Analyzing the structure of Pd-PEPPSI-*i*Pr, 3-chloropyridine is considered as a stabilizer that dispatches before Pd enters the catalytic cycle.<sup>[31]</sup> Additionally, it had been reported that the pyridine moiety can inhibit the Pd catalyst reactivity by re-coordinating onto the Pd center.<sup>[32]</sup> Based on this, we screened both 3-chloropyridine and pyridine and found that only pyridine possesses an inhibitory effect on the undesired step-growth side reaction. We believe that this phenomenon arises from the stronger coordinating effect of pyridine *vs.* 3-chloropyridine. The chloride atom decreases the nucleophilicity of nitrogen by reducing the electron density on the pyridine ring. With 1 equivalent pyridine in the Ag–Pd dual catalyst system, Pd activation on C–H bonds was successfully eliminated and the controlled living polymerization was restored. This dual catalytic system shows advantages regarding dispersity and batch variation over other direct arylation polymerization (DARp) conditions *via* concerted metalation deprotonation (CMD). The latter follows a step-growth mechanism and produces polymers with large molecular weight dispersity.<sup>[13,33]</sup> For example, in 2010 Ozawa *et al.* reported the direct arylation polymerization of regioregular P3HT *via* a Pd catalyzed DARp.<sup>[34]</sup> Though this process eliminated the use of an air sensitive organometallic reagent, this condition does not follow a chain growth mechanism, resulting in polymers with relatively high dispersity ( $\bar{D} > 2$ ), which is not beneficial to product consistency between batches.



**Scheme 6.** Proposed dual-catalytic cycles for P3HT synthesis.



**Scheme 7.** One-pot synthesis of P3HT *via* C–H activation.

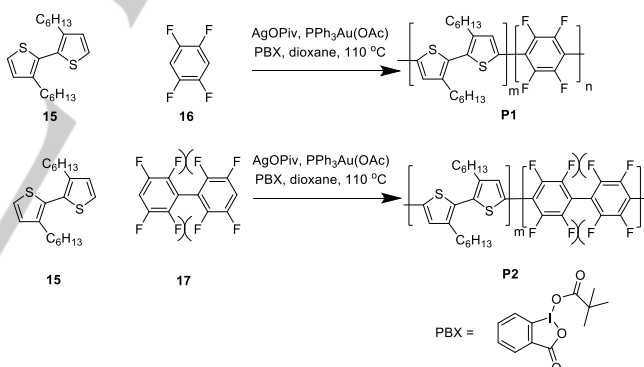
### 3.3. Donor-Acceptor Conjugated Polymer Synthesis via Dehydrogenative Coupling

Until now, the discussion has focused on P3HT, a medium bandgap polymer strongly absorbing sunlight with wavelengths from 400 to 650 nm. To harvest more energy in the solar spectrum, a low-bandgap polymer is required to harvest sunlight of wavelengths over 650 nm. Donor-acceptor alternating copolymer is a commonly used design to produce a low-bandgap light absorber. Unfortunately, to access these materials, Stille polymerization is typically used.<sup>[5,12]</sup> The use of DARp in D-A conjugated polymer synthesis is increasing. In 2016 Marks *et al.* reported a catalyst system that could significantly reduce structural defects in synthesized polymers. In this modified system, pivalic acid, a commonly applied additive in the CMD process, was substituted by 2,2-diethylhexanoic acid, a more bulky additive, which can optimize site selectivity *via* steric hindrance effects. The resulting polymers showed comparable performance in OSC applications to identical polymers that were synthesized *via* Stille coupling.<sup>[35]</sup> Leclerc *et al.* developed an impressively robust DARp catalyst system, which shows outstanding stability against oxygen and water and produces polymers with high molecular weights.<sup>[36]</sup>

While DARp is advantageous over traditional synthesis methods, one still needs to pre-functionalize one of the substrates to perform polymerization. To completely bypass those pre-functionalization steps and reduce the amount of toxic waste, cross dehydrogenative coupling (CDC) is applied to synthesize conjugated polymers from unfunctionalized monomers. Compared to electrochemical and chemical oxidative coupling polymerizations realized by electrical and chemical oxidants, CDC shows a higher controllability in the mechanism by suppressing side reactions. This results in polymers with significantly reduced concentration of defects. In electrochemical or chemical oxidative coupling, cations or radicals are generated after oxidation of a substrate.<sup>[37]</sup> These highly reactive species lead to various side reactions, and thus products with high defect concentrations. However in CDC, substrates are not oxidized – instead, the metallic catalyst centers are. For example, in some CDC system, Pd(0) is generated after reductive elimination along with the formation of a coupled product; Pd(0) is subsequently oxidized to Pd(II) and enters the catalytic cycle again. In this manner, the highly reactive cation and radical species are excluded and thus reactions become more controllable. Initially, CDC was mostly used for the synthesis of homopolymers. Recently, advances in catalyst systems have made it possible for CDC to synthesize alternating polymers. In 2018, Lu and Chen *et al.* developed a system to synthesize alternating copolymers with 3,3'-bis-(octylsulfonyl)-2,2'-bithiophene as one of the substrates.<sup>[38]</sup> Kanbara *et al.* succeeded in developing a system for the synthesis of an alternating polymer based on 3,3'-dihexyl-2,2'-bithiophene as the electron-rich monomer (**15**) and 2,2',3,3',5,5',6,6'-octafluorobiphenyl (**17**).<sup>[39]</sup> The alternating structures of these polymers were confirmed by NMR studies. At this moment, the synthesis of copolymers *via* CDC is still substrate dependent, and thus possible improvements remain.

Though limited in number, the substrates available show potential in OSC applications. Sulfonyl thiophene has been applied as a strong acceptor for a high performance D-A polymer.<sup>[40]</sup> Fluorine atoms, often introduced in these substrates, have proven able to significantly increase solar cell performance by facilitating a more planar backbone arrangement, and stronger intermolecular packing, leading to a higher charge mobility.<sup>[41]</sup> However, the mechanism of CDC is yet to be fully understood. For example, the role of silver salts in C-H activation is currently under debate; they have been proposed as an oxidant, a ligand source, halide scavenger and/or C-H activating reagent.<sup>[42]</sup> Answering this question would be necessary to further advance this polymerization method.

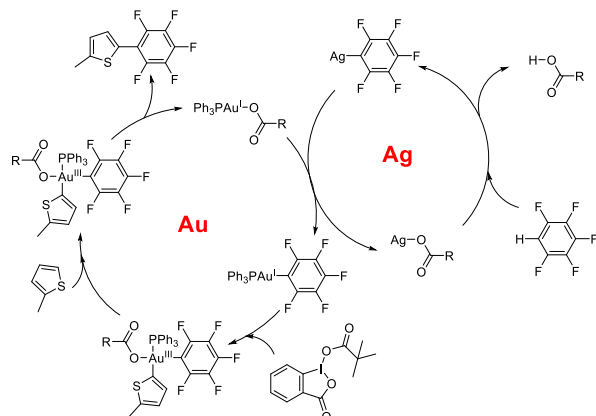
Recently by investigating a bi-metallic CDC polymerization system, we provided further experimental support to the suggestion that Ag is playing a role in the C-H activation. *Via* Ag/Au catalyst system, we succeeded in producing conjugated polymers with 3,3'-dihexyl-2,2'-bithiophene as the electron-rich monomer (**15**) and 1,2,4,5-tetrafluorobenzene (**16**) or 2,2',3,3',5,5',6,6'-octafluorobiphenyl (**17**) as the electron-poor monomer (see **Scheme 8**). However, the polymers obtained have relatively lower molecular weights, 5100 for **P1** and 9400 for **P2**, with percent alternation of around 70% throughout the polymerization process. MALDI data shows that more bithiophene units are incorporated into the backbone than the fluorinated benzene units.<sup>[43]</sup>



**Scheme 8.** Polymerization reaction scheme with 1,2,4,5-tetrafluorobenzene and with 2,2',3,3',5,5',6,6'-octafluorobiphenyl as the electron-poor monomer.

To understand the origin of this degree of alternation, deuterium studies and model studies were carried out. These experiments showed that Au(III) has a strong preference to activate thiophene while being inert to pentafluorobenzene, while Au(I) showed low reactivity to both thiophene and pentafluorobenzene. Ag, however, was found to be reactive towards electron withdrawing species and electron donating species, with stronger preference to the former. Based on these observations, we proposed bi-metallic catalysis mechanism as shown in **Scheme 9**. The homo coupling of bithiophene units in the polymers originates in the Ag cycle, where the pentafluorobenzene is replaced by thiophene. Moreover, in the polymers we noticed a greater degree of homocoupling between thiophenes than in small molecule prototypes. When bithiophene

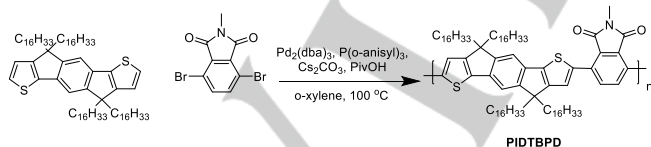
is coupled with fluorinated benzene species, it is more reactive in the Ag cycles, because of electron withdrawing effect of the fluorinated benzene species. Optimization of this catalyst system is still on going in our lab – we are developing ligands that could increase the turnover and orthogonal selectivity.



**Scheme 9.** Proposed mechanisms for dual-metallic CDC by Luscombe *et al.*

### 3.4. Further Polymer Functionalization via DARP

Besides simplifying material productions, it is also necessary to optimize material processibility toward large scale manufacturability. Conjugated polymers must have the flexibility to remain undamaged during both the roll-to-roll process and the mechanical forces applied when they are in service. Lactam and diimides are well-studied moieties in OSCs because they can modify intermolecular interactions and packing of the resulting polymers and thus increase device performance.<sup>[44]</sup> Based on a diimide moiety, we synthesized a rubbery conjugated polymer PIDTBPD (**Scheme 10**) *via* DARP.<sup>[45]</sup> The polymer demonstrates crack-onset strains of over 100%, with a decent charge mobility of  $0.06 \pm 0.03 \text{ cm}^2/\text{V}\cdot\text{s}$ . This polymer shows potential for fabricating stretchable electronic devices. The ductility is ascribed to the kinked backbone structure of PIDTBPD, which leads to weak intermolecular interaction and thus remaining mostly amorphous in solid state.



**Scheme 10.** Synthesis of PIDTBPD.

## 4. Recent Efforts on Green Solvent Processing

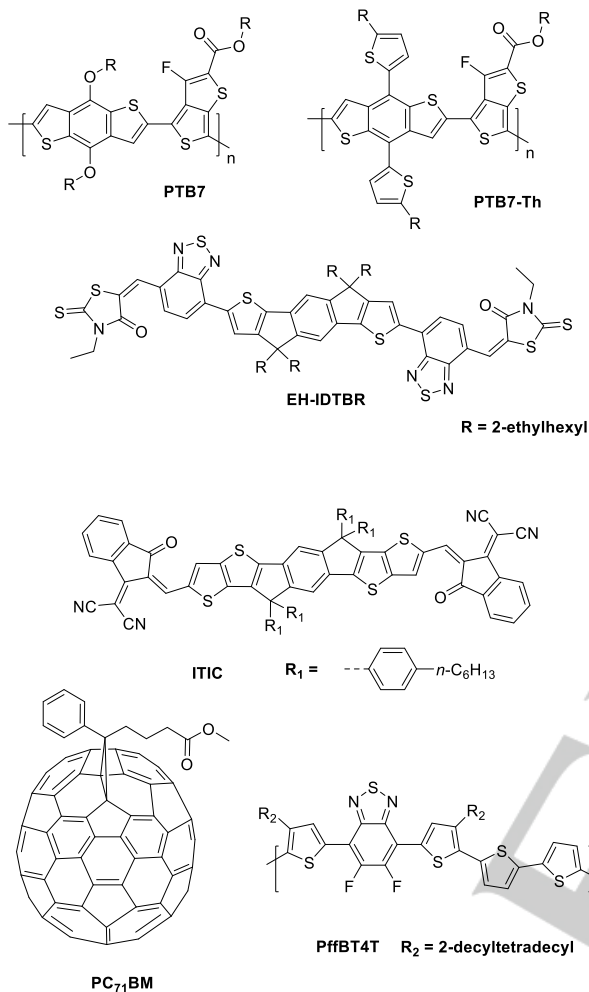
In addition to greener synthetic methods, greener processing methods are equally important for future large-scale production. Halogenated solvents such as 1,2-dichlorobenzene

(*o*-DCB), chlorobenzene (CB) and chloroform (CF) are extensively used in lab to fabricate OSCs with high PCEs, because they can promote the formation of good morphology to facilitate charge separation.<sup>[46]</sup> In 2006, Bazan *et al.* discovered that by adding alkyl thiol molecules to the P3HT/fullerene solution as additive prior to spin coating, P3HT is more orderly packed in the spincoated film, leading to a higher charge mobility.<sup>[47]</sup> In their follow-up studies, difference additives were investigated regarding morphology and PCE improvement; and they found that 1,8-diiodooctane (DIO) gave the most promising results.<sup>[48]</sup> DIO has been widely applied in OSC fabrication ever since.<sup>[48]</sup>

However, the toxicity of the solvents used in OSC processing is not a welcome characteristic for industrial usage, and researchers have been investing time in making OSCs with green non-halogenated solvents. Recent works demonstrate high PCEs of around 10% while using different green solvents, such as tetrahydrofuran (THF),<sup>[49]</sup> 2-methyltetrahydrofuran (2MeTHF),<sup>[50]</sup> toluene,<sup>[51]</sup> *o*-xylene,<sup>[52]</sup> and 2-methylanisole.<sup>[53]</sup>

Besides performance enhancements, recent studies have shown non-halogenated solvents possess other advantages. Roman *et al.* showed the thin films of PTB7-Th:ITIC (structures shown in **Scheme 11**) is less dense when spincoated in 2-methylanisole in comparison to *o*-DCB.<sup>[54]</sup> The larger distance between donor and acceptor lowers the energy of the charge transfer state, increasing the  $J_{sc}$  and decreasing  $V_{oc}$ . Thus their performances (5.36%) are nearly unchanged by comparison with those made from *o*-DCB (5.9%). In a study by Wadsworth *et al.*, devices of PffBT4T:EH-IDTBR (**Scheme 11**) processed with mesitylene, *o*-xylene and trimethylbenzene showed higher reproducibility of PCEs over ones with CB, and performances slightly higher than ones with CB as well.<sup>[52a]</sup> As for non-halogenated solvents, the thin film processing is usually performed at room temperature. However, CB usually requires elevated processing temperatures to form a uniform thin film because of the high viscosity of the polymer solution in CB. Studies have pointed out that polymer aggregations are very sensitive to temperature in CB solution, which will further lead to variation of thin film morphology, especially in large-area samples.<sup>[55]</sup> It is concluded that this sensitivity to processing temperature is the reason behind its lower reproducibility. Some high boiling point green solvents can also serve as an additive in solution processing, which is beneficial to further improve the PCE *via* green processing. For example, Colsmann *et al.* demonstrated that by doping *p*-anisaldehyde into *o*-xylene, the resulting spincoated film of PTB7:PC<sub>71</sub>BM showed improved PCE compared to ones processed by CB with DIO, 8.3% vs. 7.5%.<sup>[56]</sup> They further tested this solvent system with other blends, such as PTB7-Th:PC<sub>71</sub>BM and PffBT4T:PC<sub>71</sub>BM (**Scheme 11**), and they all showed higher PCEs compared to their halogenated solvent processed references. They explained that the enhancement in efficiency could be ascribed to a more efficient charge extraction owing to optimized film morphology when processed by *o*-xylene with *p*-anisaldehyde.

In our recent study, we investigated how solvents affect the stability of PBT7 and PBT7-Th.<sup>[57]</sup> Stability was investigated *via* the photobleaching of PBT7 and PBT7-Th thin films spincoated with CB with 3% DIO. We found that the residual solvents left in



**Scheme 11.** Structures of high performance compounds for OSCs.

as-cast films can significantly undermine the photostability of the active layers. Increased stability was observed after treating as-cast films with high vacuum for 2 hours. Residual solvent provided pathways for oxygen molecules to diffuse into the active layer, oxidizing and cleaving polymer backbones. In Fourier-transform infrared spectroscopy (FTIR), we observed signals of newly formed carbonyl groups increased as time proceeded, along with the decreasing signals of aromatic carbon-carbon double bonds.

Thus solvents with high boiling points can be detrimental to device stability because they are hard to remove completely from devices, unless high vacuum is applied, which is not realistic for the roll-to-roll printing technique. To find a solvent system that gives devices enhanced stability, we later conducted a solvent screening regarding photobleaching rate of polymer films, and a trend was observed - photobleaching rate increases as boiling

point increases. *o*-Xylene and *N*-methyl-2-pyrrolidone (NMP), two solvents with relatively lower boiling points slightly over 200°C, gave dramatic improvement in film stability against photobleaching. Despite the relatively lower boiling point of NMP, it is still able to deliver desirable morphology by reducing fullerene aggregation, confirmed by atomic force microscopy (AFM). This is a significant advancement in developing greener and low-cost processing conditions. Plus, this technique can be used in roll-to-roll printing to fabricate devices with stable performance. Their low boiling points enable the complete removal of residual solvents without high vacuum condition.

Recently, Machui *et al.* has successfully utilized 2-methylanisole to fabricate semitransparent modules consisting of P3HT:EH-IDTBR with area of 59.52 cm<sup>2</sup> *via* the doctor blading technique. Compare to small area devices made from spin coating, these modules show a slight decrease in PCE, from 5.41% to 4.70%.<sup>[58]</sup> This shows a promising future of fabricating OSCs in an industrial scale. By being environmentally friendly and enhancing efficiency and stability, using green solvents for processing can solve several problems hindering the commercialization of OSCs.

## 5. Conclusion and Outlook

In this year, huge breakthroughs on OSCs have been achieved regarding PCEs. With optimized device designs, OSCs can be competitive and profitable. On the perspective of sustainable economy, lab-scale manufacturing methods we are now using, however, are serving as obstacles to our vision of OSCs going into market, because of the toxic or dangerous chemicals involved. An increasing number of researchers are now focusing on these issues, and yet there are still challenges that remain. 1) At this moment, polymers produced *via* direct arylation may suffer from defects, such as undesired branching and homocoupling, which are detrimental to device performance. Branching can significantly undermine molecular packing and leads to a reduced charge mobility. Homocoupling can generate trap sites, which increases recombination of charges and decreases charge mobility. Homocoupling will also results in lower  $V_{oc}$  and thus lower PCE.<sup>[59]</sup> This requires us to develop catalyst system will higher site selectivity. 2) Industrial enforceability should be considered seriously when designing new high performance materials - shorter synthesis, less pollution and enhanced operability in material synthesis and device fabrication. The longer the synthetic route is, the higher the cost of the device, undermining the market competitiveness of the final product. Toxic reagents such as halogenated solvents and organotin compounds should be avoided. We look forward to the day we can eliminate the use of organotin and other toxic compounds in OSC production. 3) The stability of OSCs is yet to be improved. The instability is due to the oxygen sensitive nature of organic semiconductors to a large extent,<sup>[60b]</sup> and thus efforts are needed to develop materials that are less air sensitive. Appropriate encapsulation is proven feasible to give devices with a more reasonable lifetime for future application.<sup>[10, 60]</sup> With

combined efforts, we can develop OSCs with market viability in the near future.

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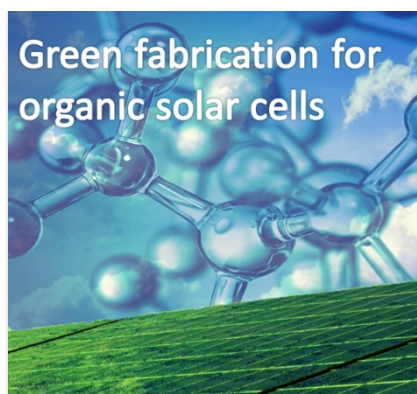
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Layout 1:

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As a green energy solution, organic solar cells have attracted world-wide attention in past decades. With power conversion efficiency records as high as 17%, its industrial profile should be now taken into perspective. In this account, we will share our thinking and research regarding different aspects on the industrialization of organic solar cells, such as economic and environmental profiles, and polymer synthesis and device fabrication optimization.

*Yunping Huang, Christine K. Luscombe\****Page No. – Page No.****Towards Green Synthesis and Processing of Organic Solar Cells**

Layout 2:

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