The Development of Conjugated Polymers as the Cornerstone of Organic Electronics

Robert M. Pankow[a] *and Barry C. Thompson*[a]*

[a]Department of Chemistry and Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, California 90089-1661.

ABSTRACT. The expansion of the field of organic electronics has hinged upon structural and fundamental developments in the field of conjugated polymers. Conjugated polymers allow for the manufacture of low-cost, light-weight, flexible organic electronic devices, with notable applications in organic photovoltaics (OPV), organic field effect transistors (OFET), and organic light emitting diodes (OLED). This extraordinary breadth of applications is due to the remarkable diversity of structure, an extensive understanding of structure-function relationships, and the relative ease of structural tuning. Important advancements and the development of such applications is largely due to the evolution of polymer structure, enabled by a broad range of synthetic methods for the tailoring of structures and the development of improved polymerization conditions to limit defects. This perspective provides background from the early days of concerted and focused conjugated polymer research (1970s-1990) to the present, and describes how the tailoring of conjugated polymer structure has now become closely tied to application. A significant focus is also directed to how polymerization methods have evolved from the aggressive, unselective conditions used for oxidative polymerizations to finely tuned transition-metal catalyzed polymerizations that can provide incredibly high structural-fidelity and can proceed through C-H activation. Areas for future work and emerging areas are also discussed, such as high-performing polymers without added structural and synthetic complexity, identifying polymer structures with improved environmental stability, flexible and transient or bioresorbable conjugated polymers, mixed-ion conductors, and photocatalytic and select biological applications.

1. Introduction.

Conjugated polymers are a unique class of polymer that have been designed for use in a broad range of electronic applications due to their semiconducting, conducting, electrochemical, and/or optical properties. They provide an alternative to inorganic materials since they are relatively low-cost, can be solution processed allowing for roll-to-roll (R2R) processing, and can be fabricated in lightweight and flexible device applications.[1] The synthetic tunability of conjugated polymers allows the electronic and physical properties to be extensively optimized. Their physical properties, such as solubility and crystallinity, and electronic properties, such as charge transport and light absorption, can be tuned through synthetic modification. This has allowed them to find successful application in devices, such as organic photovoltaics (OPV), organic field effect transistors (OFET), and organic light emitting diodes (OLED), which will be the applications primarily discussed in this perspective.[2–5] Additionally, their synthetic flexibility and tunability allows them be incorporated into other uses, such as electrochromic devices, chemical sensors, organic lasers, and biological applications, which will not be discussed in detail, but relevant reviews are supplied for the reader’s interest.[6–9]

While the initial pursuit of knowledge for conjugated polymers was on their fundamental properties, such as conductivity, electrochemistry, and photophysical properties, it evolved over

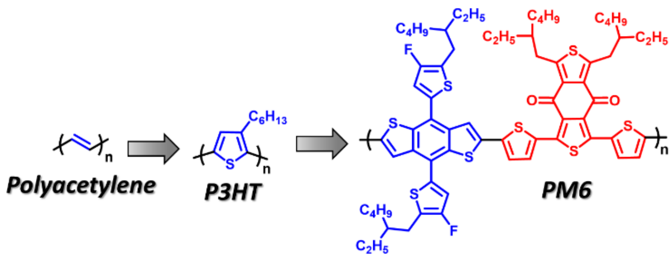


Figure 1. From the simple repeat unit of polyacetylene, to the synthetic undertaking to prepare regioregular P3HT, and to the structural complexity of 2D-conjugated polymers, such as PM6, it can be seen how much conjugated polymer structure has progressed in recent decades.

the decades to understanding how minute changes in the structure impact the performance for a given application. Thus, the architectural progression and development of conjugated polymers from simple repeat units, such as from the simplest conjugated repeat unit, found with polyacetylene, to poly(3-hexylthiophene-2,5-diyl) (P3HT), and to PM6 (see Figure 1), was anything but slow and steady throughout the decades.[10] Bursts of new developments within the field of conjugated polymers came hand-in-hand with advancements in organic synthesis, allowing for the tailoring of new polymer structures. These were also often coupled with advancements in the understanding of operating mechanisms for given organic electronic applications, and so structural advancements in conjugated polymers were largely application driven and being based on how polymer design influenced device performance. As outlined in Figure 1, important structural developments in the field of conjugated polymers include the improvement of polymerization conditions to prepare polymers with high structural fidelity, e.g. regioregular P3HT and donor-acceptor copolymers (PM6), the tuning of electronic and physical properties through the addition heteroatoms along the π-conjugated backbone, such as fluorine, the introduction of sidechains for improving solubility or tailoring physical properties, and more advanced architectures, such as perfectly alternating donor-acceptor copolymers. Additionally, it can be seen with PM6 (Figure 1) how polymers began to include fused-rings and extended, 2-dimensional conjugation.

In this perspective article, we will illustrate the connections of the historical underpinnings of the field of conjugated polymers to the present state-of-the-art. We focus on significant breakthroughs in the synthetic chemistry that have led to the macromolecular architectures of current interest, and we draw correlations to the physical and electronic properties and cutting-edge applications that are thus enabled. In order to clearly emphasize and articulate the structural progression for many of the conjugated polymer structures presented, a red and blue coloring system is used for the figures. The color blue will be used primarily to indicate a homopolymer or a donor portion of a donor-acceptor copolymer with red used to emphasize a particular structural feature within, and red will be primarily used for the acceptor portion of a donor-acceptor copolymer with blue used to emphasize a particular structural feature within. However, this perspective will not discuss the fundamental principles associated with the electronic structure of conjugated polymers or device operation, and so the reader is directed to relevant reviews on that subject.[4,11–15] Finally, we will survey outstanding challenges in the field and highlight significant directions for future development. It is important to note that given the broad structural diversity and various applications of conjugated polymers, some structures and applications, while significant, are not mentioned or discussed for concision, and so at those points the reader is directed to relevant reviews.

2. 1970-1990: Historical Development of Conjugated Polymers.

2.1 Conjugated Polymer Structure from 1970-1990

Although the historical development of conjugated polymers spans over a century, the emergence and expansion of conjugated polymers as a unique and concerted field of study is much more condensed to recent decades. Since the historical development of conjugated polymers has been reviewed extensively, it will not be covered in great detail here.[16–20] Conjugated polymers have been known since 1834, but were studied in only a sporadic and isolated fashion until the 1970's. The increased interest and focused effort in the 1970s for the field of conjugated polymers originates from the work of conducting polymers, i.e. synthetic metals. Specifically, the work of Labes on the inorganic polymer, poly(sulfur nitride), served as an inspiration for the seminal work by MacDiarmid, Heeger, and Shirakawa detailing the doping of polyacetylene (Figure 2A), which served as an inspiration for the concerted field of research on conjugated polymers.[21–23] The findings of MacDiarmid, Heeger, and Shirakawa lead to the enhanced study of the early generation of conjugated polymers (Figure 2A) (some of which had been historically known), which are comparatively minimalistic compared to the exotic structures of the present conjugated polymers (compare to PM6 in Figure 1). Simple repeat units, such as polyaniline (PANI), polypyrrole (PPy), poly(paraphenylene) (PPP), and poly(paraphenylenevinylene) (PPV) were state-of-the art during the early stages of the field.[17] This simplicity can be attributed to limited development of structure-function relationships for conjugated polymers where the directive for these materials was primarily to understand their metallic states achieved by various doping mechanisms, and at that time there was still much information to be garnered from studying these relatively simple structures. Perhaps more importantly, these simple polymers can be easily prepared from simple commercially available starting materials, such as aniline for polyaniline (PANI) or thiophene for polythiophene (PT, Figure 2A).[24] Furthering this point, the structural simplicity could also be attributed to limitations in the strategies for monomer and polymer synthesis. In many ways, advancements within the field of organic electronics have been tethered to advancements in organic and polymer synthesis.

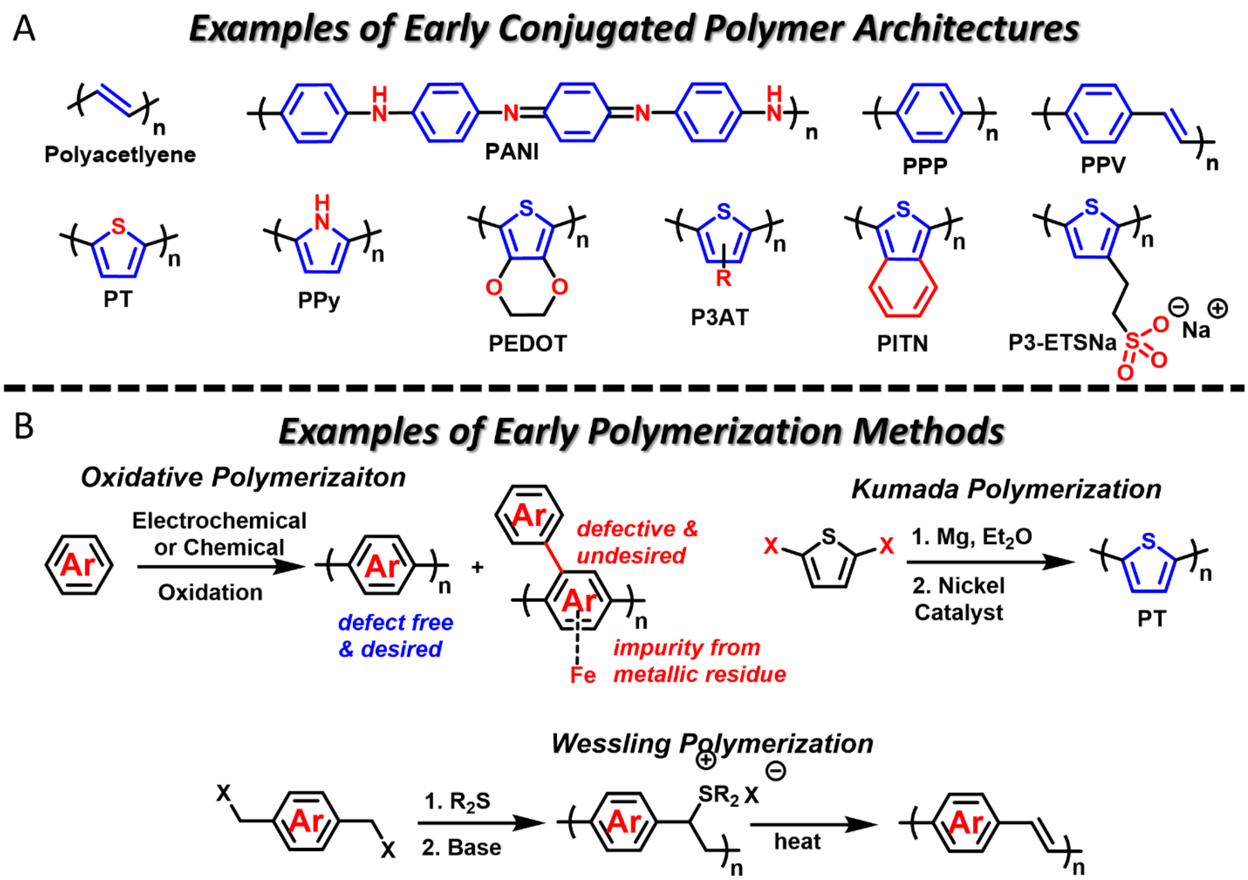


Figure 2. (A) Examples of early conjugated polymer structures commonly studied from in the 1970s-1990. (B) Examples of early polymerization methods, although not an exhaustive list.

During the early stages of the field in the 1980's, many important and transformative contributions were provided from the collaborative efforts of Heeger and Wudl.[25,26] Pioneering studies, such as the spectroscopic characterization of poly(alkylthiophenes) (P3AT), water soluble conjugated polymers (P3ETS-Na), and the synthesis of the first narrow bandgap polymer, poly(isothianapthene) (PITN), shown in Figure 1, were a result of this collaboration.[27–30] This collaboration afforded many critical discoveries and studies that enabled the field of conjugated polymers to flourish and inspired researchers across various fields of science, such as physics, chemistry, and engineering, to enter and contribute to a still emerging and developing field. It is important to note, that during this time (1970-1990) the field of conjugated polymers was rather limited as an exploratory area, where practical applications of these materials had not been widely realized, such as in organic electronic devices.

At the time, the common metric for the characterization of conjugated polymers was measurement of the conductivity in the doped state. The use of conductivity for evaluating a new polymer reflects the trend for discovering synthetic metals, as the discovery of semiconductor applications such as OPV, OLED, or OFET had not occurred yet. For reference, Heeger et al. reported conductivities of 220 S/cm, 14 S/cm, and 0.4 S/cm for polyacetylene, polythiophene, and PITN.[21,28,29] These were performed using oxidized polymer films in the presence of the dopants AsF_5 (polyacetylene and polythiophene) and bromine (PITN).

A polymer from Figure 2 that continually finds new interest and application from its original disclosure in patent by Bayer A.-G. in 1989 is poly(3,4-ethylenedioxythiophene), PEDOT.[31,32] This polymer was prepared using chemical oxidation with anhydrous $FeCl_3$, affording polymer films with conductivities of 2.3 S/cm, as reported in the aforementioned patent. More extensive characterization for PEDOT and its derivatives occurred in the following decade, and so they are discussed more extensively in the next section.

2.2 Polymerization Methods from 1970-1990

As mentioned, synthetic procedures, including the polymerization conditions, for conjugated polymer synthesis were incredibly limited during the early stages of study (1970s-1990). Polymerization conditions were mostly limited to electrochemical polymerizations, chemical oxidative polymerizations, such as employing anhydrous $FeCl_3$ as the chemical oxidant, or through the application of name-reactions, such as Wittig, Gilch, McMurry, Kumada cross-coupling, and Wessling reactions.[24,33–39] Polyacetylene and its derivatives could be prepared using Ziegler-Natta polymerization.[40] These methods very often laced the resulting conjugated polymer product with defects, either due to low regio- or chemo-selectivity, as shown in Figure 2B, or due to intermediate steps within the synthesis not reaching completion before isolation of the polymer. It should also be noted that the monomer synthesis, such as with using the Wessling reaction, required extended synthetic pathways in order to install the reactive functionality. The scope and functional group tolerance was also limited, due to the often-harsh conditions for certain polymerizations. The 1970s saw a growth in the application of organometallic chemistry to aryl cross-coupling reactions. The application of these towards the synthesis of conjugated polymers was inevitable, such as the use of Kumada cross-coupling, which was originally disclosed by Yamamoto et al. (Figure 2B).[28,41,42] The impact of Yamamoto's application of transition metal catalyzed cross-coupling reactions cannot be overstated, and readers are directed to a mini-review summarizing these contributions.[43] This cross-coupling revolution opened a new door towards polymers with improved structural fidelity relative to what was provided with the aforementioned polymerization methods.

3. 1990-2000: Accessing Well-Defined Polymers

As a result of the fundamental work that defined the 1980's, the following decade saw a flourishing field, largely due to the development of the first organic electronic devices and the improvement and expansion of synthetic methodologies for the polymerization and functionalization of conjugated polymers. In the process, the field saw a dedicated pursuit of new polymer architectures in order to advance understanding of fundamental structure-property relationships, as well as to optimize materials for specific applications. However, at this time (1990-2000) a growing fraction of the work on conjugated polymers was focused on their introduction into new organic electronic applications. Specifically, during the 1990's conjugated polymers began to be implemented into a variety of applications, such as in OPV, OLED, and

OFET devices or in chemical sensor, electrochromic, and organic laser applications.[6,7,9,11,44,45] This broad range of applications could be attributed to the promise of conjugated polymers at potentially providing low cost alternatives, both in synthesis and processing, as well as desirable mechanical properties compared to their inorganic counterparts. Since there are extensive reviews on the subject of device and conjugated polymer applications, the reader is directed towards these for further elaboration on the device physics and working principles.[7,9,33,44,46–48].

3.1 The Development of Application Focused Design: Conjugated Polymer Structure from 1990-2000 for OLED and OFET Applications

Of the various aforementioned applications, a primary focus of conjugated polymer research in the 1990s was in the development of new emitters for OLEDs, which followed the seminal work by Burroughes et al. describing the fabrication of an OLED device incorporating PPV (Figure 2A).[49] Following-up this initial report, the research groups of Friend and Holmes provided many additional important advancements within this area.[50–54] Condensed into simplified terms, the general design criteria for polymers in OLED applications was high luminescence in solution or as films, a useful although not always accurate diagnostic before fabrication of a device, and an amorphous morphology in order to avoid the aggregation induced quenching through interchain interactions.[55–58] The use of different aryl units, substituents, and inclusion of heteroatoms (Figure 3A) allowed for tuning the physical properties, such as solubility and morphology, and also electronic properties, such as the bandgap, influencing the color and intensity of emission. Shortly thereafter, a critical and revolutionary development for the field of conjugated polymers was the report of the polymer MEH-PPV by Wudl and coworkers (Figure 3A).[59] This polymer, although structurally similar to its parent-analog, PPV, was a major

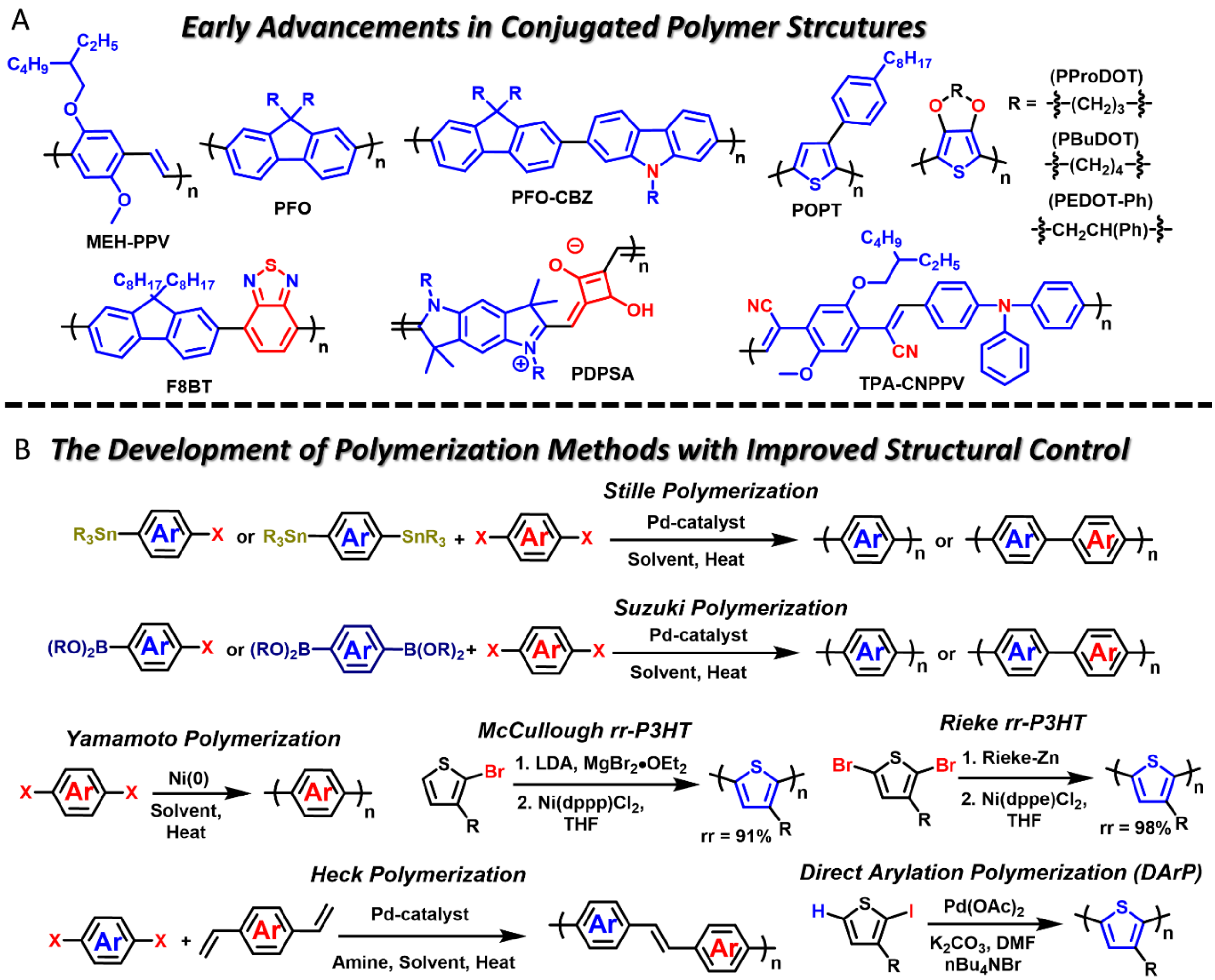


Figure 3. (A) Advancements in the conjugated polymers in the 1990s relative to the previous decades is exemplified with the inclusion of new repeat units and alkyl substituents for improved solubility. (B) A key development within the decade of the 1990s was the application of various transition-metal catalyzed cross-coupling reactions toward the synthesis of conjugated polymers, improving the structural fidelity of the polymer and limiting undesired defects.

advancement in that it incorporated branched alkyl substituents, an early example of side-chain engineering, rather than the often encountered linear alkyl substituents. This allowed for increased interchain polymer distance and an amorphous arrangement of polymer chains.[60] These substituents also allowed for facile solution processing, which is critical for thorough structural characterization and an important attribute for the low-cost manufacture of display devices. MEH-PPV became one of the most studied polymers over the following decade. A pioneering study by Holmes and Friend et al. detailed a blend of MEH-PPV and the polymer acceptor CN-PPV into a photovoltaic device.[52] Around the same time, Wudl and Heeger disclosed the development of the polymer-fullerene solar cell with their study of a blend of MEH-PPV and the fullerene, C_{60}.[61,62] These important contributions would ignite the field of research for conjugated polymer in OPV, and it would signal a shift in the next decade from heavily studying OLED to more focus on OPV.

Another important class of conjugated polymers studied at the time were polyfluorenes, such as PFO, PFO-CBz, and F8BT (Figure 3A). These polymers incorporated a fused biphenyl with the inclusion of a quaternary carbon, which allowed for the facile inclusion of a variety of solubilizing groups. Additionally, these materials are highly-emissive making them desirable for OLED applications.[46,63,64] The fused repeat units of fluorene allow for extended conjugation along the polymer backbone with the inclusion of solubilizing alkyl substituents, which had led to a twisted conformation with the non-fused phenylene based polymers.[55] Polymers incorporating the fluorene unit also displayed good charge carrier mobilities, allowing them to be incorporated into OFET devices.[65] The design of polymers for OFET applications was in contrast to that of OLEDs. Specifically, polymers with crystalline properties were desired, such as polythiophenes or polyfluorenes, which allowed for improved charge transport along and between polymer chains.[65–67]

Aside from the aforementioned polymers (primarily homopolymers), a critical contribution from this time period was the development of the donor-acceptor copolymer, which is based upon the work of Havinga. In the seminal report, the synthesis of copolymers through the condensation of squaric acid and a series of pyrrolines, such as PDPSA in Figure 3A, is described.[68,69] While conjugated polymers incorporating electron-deficient and electron-rich units had been reported, the concept of using a donor-acceptor copolymer to modify the electronic properties, such as the bandgap, had not been realized.[70] The idea of using donor-acceptor copolymers to modulate the bandgap was an important contribution for furthering the development of new polymer architectures for OPV applications, and would be a major research focus for the following decade. Polythiophenes were also receiving increased attention as well, since the structural tuning of the monomers could be easily accomplished allowing for a broad range of electronic properties, with POPT as an example (Figure 3A).[71,72] Additionally, important achievements were made to improve the regioregularity of this class of polymers through improvements in the synthetic methods, which is further discussed below.

In addition to P3ATs, the synthesis and characterization of PEDOT (Figure 2) and its analogues, shown in Figure 3A with PProDOT, PBuDOT, and PEDOT-Ph, greatly expanded.[72–77] During this decade, Reynolds contributed many notable works relating to the synthesis and characterization of analogs of PEDOT, which is detailed in a review relevant to the time period.[24] The major underlying interest for this class of materials was in electrochromic applications, due to the highly tunable bandgap allowing for a broad spectrum of colors for polymer thin-films. Additionally, these polymers possess low-oxidation potentials, long-term electrochemical switching, and good environmental stability. These properties can be attributed to the molecular design of the repeat unit where the electron-donating oxygens serve to stabilize the oxidized form of the polymer. To show how structural modification altered the electrochromic and conductivity properties, Reynolds et al. compared PEDOT, PProDOT, PBuDOT, and PEDOT-Ph.[72] It was found that the switching time and conductivity varied from 2.2 sec (for both PEDOT and PProDOT), 1.3 sec, and 0.8 sec, respectively. For *in situ* conductivity measurements of the electrochemically oxidized polymers, it was found that PEDOT, PProDOT, PBuDOT, and PEDOT-Ph afforded conductivities of 8.6, 12.1, 0.2, and 1.2 S/cm, respectively.

3.2 Polymerization Methods from 1990-2000

Enabling this transition of conjugated polymers from primarily a laboratory interest to a practical setting was the implementation of transition metal catalyzed cross-coupling reactions, such as Suzuki-Miaura (Suzuki), Heck, Yamamoto, and Migita-Stille (Stille), for polymer synthesis (see Figure 3B).[37,78–85] Developing polymerization conditions based on the Stille or Suzuki reactions, for example, was critical because many of the previous polymerization conditions used prior, such as chemical or electrochemical oxidation, gave polymer products with high levels of defects that impaired the optical and electronic properties of the corresponding polymer.[10] Additionally, methods such as Stille and Suzuki enabled the synthesis of structurally diverse conjugated copolymers, creating an avenue for accessing polymers decorated with a variety of unexplored functional groups.[86–88] In contrast, the low regio- and chemo-selectivity of chemical or electrochemical oxidation and the harsh conditions required for other polymerization methods, such as Wessling polymerization, depicted in Figure 2B, prohibited such structural diversity. Also, the inclusion of solubilizing groups allowed for high molecular weight polymers to be obtained with the aforementioned polymerization procedures. The ability to access high molecular weight polymers with minimized levels of structural defects allowed for improved device performance and more desirable physical and electronic properties through the extension of π-conjugation within and π-stacking between polymer chains.

The seminal work of Yu et al. described conditions for conjugated polymer synthesis using Stille cross-coupling, which invokes the use of an aryl dihalide, an aryl distannane, and a palladium catalyst (Figure 3B).[78,79,82,84] Stille polymerization remains one of the most widely used methods for the synthesis of conjugated polymers, because it is highly tolerant of various functional groups allowing for a broad scope of conjugated polymers to prepared. Suzuki polymerization, which had been reported for the synthesis of of PPP (Figure 2A) at the end of the 1980s, received increased attention during the 1990s as a complementary method to the other transition-metal catalyzed cross-coupling polymerizations.[37,89,90] Rather than using a toxic, trialkyl tin functionality for transmetalation, a more benign boronic acid or boronic ester is used (Figure 3B). For polymers incorporating the vinylene unit along the backbone, Heck coupling provided a convenient and relatively mild pathway for this inclusion. Importantly, this provided a new route to PPV based polymers (Figure 3B).[81,85] Yamamoto polymerization (Figure 3B) is another critical contribution, allowing for the polymerization of aryl dihalides, which greatly simplifies monomer synthesis in that the synthesis of a main-group intermediate is not necessary to promote transmetalation to the active catalyst.[91,92] Disadvantages of this polymerization method include the inability to synthesize perfectly alternating copolymers, which can be prepared using Stille, Suzuki, or Heck polymerization methods, and the need for stoichiometric amounts of Ni(0).[88]

For the synthesis of polythiophenes, which were a primary focus during this time, significant synthetic development was realized for the preparation of highly regioregular P3ATs and for the synthesis of P3ATs using C-H activation (see Figure 3B for general schemes and conditions). Regarding the former, the numerous works of Rieke and McCullough during this time were monumental for the development of the controlled synthesis of conjugated polymers. In a seminal study, McCullough disclosed conditions using Kumada coupling to polymerize 3-alkylthiophenes with various alkyl substituents, affording rr up to 91% compared to the 54%

achieved electrochemically or through chemical oxidation using anhydrous $FeCl_3$.[93] Due to the extended conjugation consequential of the higher regioregularity, the conductivities of the highly-rr P3AT were found to be 50 to 60 times higher than that of the regiorandom P3AT. Rieke et al. then followed up McCullough's work, disclosing conditions that used Negishi coupling to polymerize 2-(bromozincio)-5-bromo-3-hexylthiophene.[94] The highly reactive zinc described in this report afforded the desired monomer, 2-(bromozincio)-5-bromo-3-hexylthiophene, exclusively, which was then polymerized to afford P3HT with an rr of 98%. From these initial works, numerous contributions from Rieke, McCullough, and others followed during the time period of 1990-1999, and the reader is directed to select studies for further reading.[95–97]

For the synthesis of poly(alkylthiophenes) using C-H activation, Lemaire reported the first set of conditions just before the end of the decade for direct arylation polymerization (DArP), which is shown in Figure 3B.[98] At the time of the disclosure of this new polymerization method, it was described as Heck-type given the olefin nature of the thiophene π-bond undergoing C-H activation. Although the rr of the P3HT in Lemaire's study was only 70%, the significance of this work is that it set the stage for future conjugated polymer synthesis via DArP, which allows for circumventing the need to install a main-group intermediate is not necessary to promote transmetalation to the active catalyst. This allows for a reduction in the number of synthetic steps to access a monomer and the amount of associated chemical waste, and it can be accomplished using catalytic amounts of a transition metal catalyst unlike Yamamoto polymerizaiton. Each of the developments from McCullough, Rieke, and Lemaire for polythiophene synthesis would have significant impact on future work and the field of conjugated polymers overall.

4. 2000-2010: A Proflific Expansion of Architecture, Synthesis, and Properties.

From the pioneering work accomplished in the 1990s, the groundwork was laid for researchers in the next decade to further expand research areas regarding conjugated polymer design and synthesis. From the structural variety displayed overall in Figure 4, it is apparent that research in the area of conjugated polymers was focused on learning structure-property relationships enabled by fundamental work of the previous decades. Determining how molecular weight, semi-crystallinity, structural defects, and polymer architecture, such as with donor-acceptor copolymers, altered device performance became an underlying feature. This was enabled by the improved polymerization methods, such as Suzuki and Stille polymerizations, that allowed for high molecular weight polymers with improved structural fidelity and a broader functional group tolerance. In addition, the academic focus on applications for conjugated polymers began to shift from the primary focus of OLEDs to OPV and OFET. As such, understanding how to improve the absorption of photons rather than their emission and the fundamental studies of charge transport began to emerge through the fastidious tailoring of structure.

For OPV, this was accomplished through the pursuit of narrow bandgap materials where the energy levels were tuned to maximize photon absorption without sacrificing other aspects critical to device performance, such as charge transfer to [6,6]-phenyl-C61-butyric acid methyl ester, PCBM, or the open-circuit voltage (V_{oc}).[44,99] Specifically, it was found that bandgaps should be tuned to between 1.2 to 1.9 eV to match with the emission of the solar spectrum, lowest unoccupied molecular orbital (LUMO) energy levels should be properly offset (0.2-0.3 eV) to allow for efficient electron transfer to PCBM, which is at approximately 4.3 eV, and to avoid ambient oxidation highest occupied molecular orbital (HOMO) energy levels should be below -5.26 eV.[100] The strategy for accomplishing this synthetically was to develop structures that stabilized the quinoidal form, such as with PITN (Figure 2A), which was done using the donor-acceptor archetype developed by Havinga and discussed in the previous section. Examples of these types of donor-acceptor polymers in Figure 4 and discussed below.[101–103]

For OFET, critical developments were made in tailoring the crystallinity of polymers, lowering the HOMO energy level without significantly raising threshold voltages, and the application of donor-acceptor copolymers.[99,104] The use of the donor-acceptor interactions enforced backbone planarity, improving long-range structural order, decreased π-π stacking distances between polymer chains, allowed for fine-tuning HOMO and LUMO energy levels, and provided spatially separated alkyl substituents.[104,105] This was, of course, enabled through the increased application of organic synthesis for the functionalization of monomers where in previous decades an apparent structural simplicity was primarily observed (as shown with the polymer structures in Figures 2A and 3A). Much of this expansion of structure is also consequential of the improvement in polymerization methods, primarily with Stille and Suzuki polymerizations, which are highly tolerant of various functional groups and can afford high molecular weight polymers with good structural fidelity.

4.1 Application Driven Design: Conjugated Polymer Structures from 2000-2010 for OPV and OFET Applications

As depicted in Figure 4, polymers with ionized side chains gained increased attention due to their applications in organic electronics and biological applications, since their ionic side chains allow them to be processed in polar organic or aqueous solvent. The polymers PFN-Br and PFN-P prepared by Cao and colleagues (Figure 4) were initially synthesized as water-soluble emitters for OLED applications, although PFN-Br found more use as an interlayer in OPV devices.[106,107] Another example of water soluble polymers, which utilize the donor-acceptor copolymer architecture, is depicted with the sulfonate functionalized PPE-BTD-SO_3^- (Figure 4).

Schanze et al. demonstrated the tunable photophysical properties of these polymers in solution through the preparation of a series of PPE-based copolymers.[108]

The increased attention for polythiophenes in the 2000's was primarily due to the improvements in polymerization methods, which allowed for improved structural fidelity and therefore controllable and desirable physical and electronic properties. An example of this is the copolymer PBTTT-C14 (Figure 4), which McCulloch et al. demonstrated to have good charge-carrier mobilities of 0.2-0.6 $cm^2\ V^{-1}\ s^{-1}$ in their initial report.[109] PBTTT was an important development for OFET devices because it takes a rather simple and straightforward polythiophene architecture, but with improvements to charge mobility compared to P3HT, which can provide a mobility of 0.1 $cm^2\ V^{-1}\ s^{-1}$ with high regioregularity, for example.[110] These improvements in mobility can be attributed to the improved crystallinity consequential of the increased spatial separation of the alkyl substituents, allowing for increased side-chain interdigitation and improved long-range structural order.[111,112] From measurements of the ionization potential (IP), PBTTT possesses a higher IP at 5.1 eV compared to P3HT (4.80 eV).[109] This translates into a polymer more resistant to oxidation and therefore more stable, with a HOMO inside the typically targeted range of 5.0-5.5 eV for OFET devices.[99] Another important class of polythiophenes is illustrated with the PTB series of polymers pioneered by Yu (Figure 4), which afforded power conversion efficiencies of 5.6% when blended with PCBM.[113,114] The series of polymers based on this general architecture profoundly influenced the synthesis of conjugated polymers for OPV applications, with more examples in the following section. The functionalized thieno[3,4-b]thiophene acceptor unit was based on early work by Pomerantz et al. at the start of the decade, which described homopolymers possessing an alkylated version of the same isomer.[115] This particular isomer of thienothophene ([3,4-*b*] rather than the [3,2-*b*] found in PBTTT), stabilizes

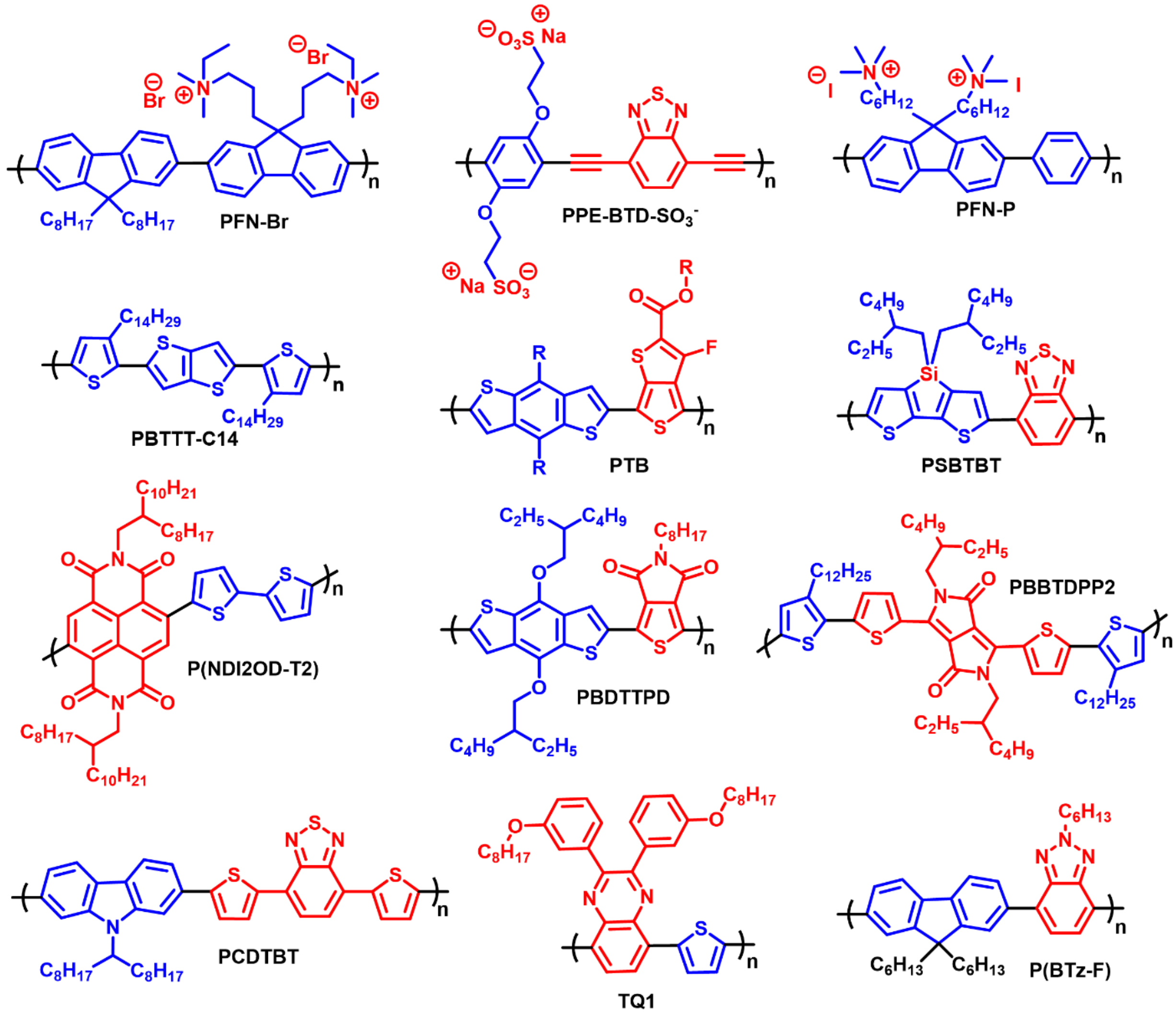


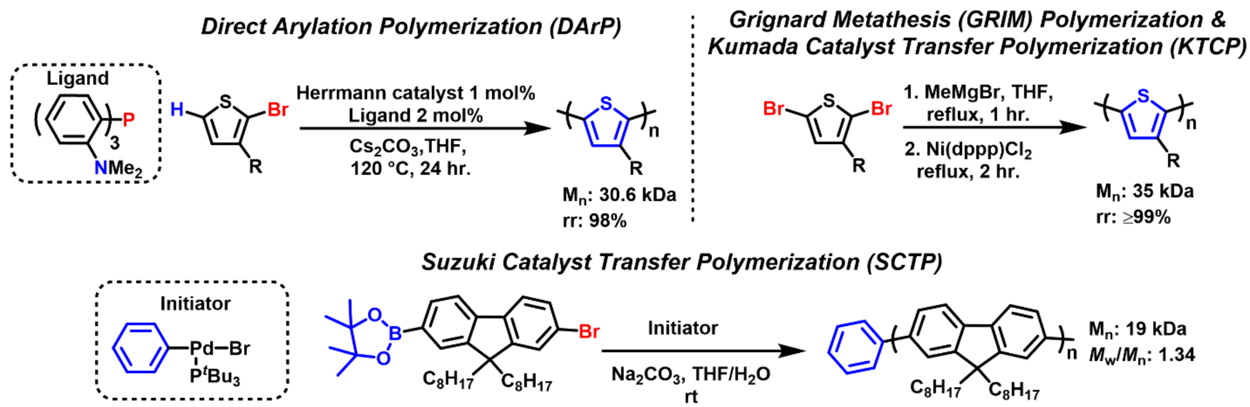
Figure 4. The explosion of structural diversity from 2000-2010 resulting from the application of many organic synthetic methods to monomer and polymer functionalization, as depicted with the examples of polyfluorenes, polythiophenes, amide and imide functionalized polymers, and azaheterocyclic compounds.

the quinoidal form thereby allowing for a very narrow bandgap and facile light absorption for the polymer.[116] These polymers also popularized the use of the benzo[1,2-b:4,5-b']dithiophene (BDT) donor, which had been incorporated into various polymer architectures beforehand, although their potential as high-performance polymers had not yet been realized.[117–120] Most importantly, the development of the PTB polymers showed how various organic synthetic methods can be used to functionalize a given monomer so as to tailor the polymer properties.[116] This judicious tuning of monomer structure to alter the polymer properties is also observed with the inclusion of main-group elements to afford fused ring-structures, such as the silolo[3,2-b:4,5-b']dithiophene in PSBTBT. Compared to the cyclopenta[2,1-b;3,4-b′]dithiophene analog, PCPDTBT, which provides efficiencies of 3.2% in polymer solar cells, the inclusion of silolo[3,2-b:4,5-b']dithiophene provides improved charge transport providing an efficiency of 5.1% for PSBTBT.[121,122] The inclusion of other main group elements, including phosphorus, selenium, tellurium, arsenic and germanium, has also been explored, but are not included in this discussion for the sake of brevity.[123–128]

With the advent of the donor-acceptor copolymer in the previous decade (1990s) and the new directive for low-band gap polymers or those with absorption extending from the visible to the near-IR, amide and imide functionalized polymers became of great interest with examples shown in Figure 4.[105] Amide and imide functionalized monomers are particularly intriguing due to the relative ease of synthesis, low lying LUMO energy levels, ambient stability, and structural variety.[101,105,105,129,130] Since these monomers can typically be realized within a few facile synthetic steps, they are excellent for screening or tailoring a variety of different polymer architectures through the incorporation of different solubilizing groups or donor units. One of the early works on narrow bandgap amide-based copolymers was provided by Janssen et al., which described a 4.0% PCE obtained with PBBTDPP2 (Figure 4) and $PC_{70}BM$.[131] Another example is the copolymer P(NDIOD-T2) or N2200, shown in Figure 4, which is a multifaceted material that was initially used for the fabrication of high-mobility transistors under ambient conditions, with mobilities ranging from 0.2-0.5 $cm^2 V^{-1} s^{-1}$, and it has more recently found use in all-polymer solar cells as an acceptor polymer providing power conversion efficiencies of over 10%.[132–134] Its efficiency at electron transport can be attributed to the ideal energy of it LUMO at -4.35 eV, which is between the generally targeted range of -3.6 to -4.5 eV, and the highly coplanar structure of the polymer backbone.[105] PBDTTPD (Figure 4), developed by Leclerc et al., is a prime example of a donor-acceptor copolymer based on the structural archetype outlined by Yu with the PTB-polymers. The polymer provides good synthetic accessibility with the TPD acceptor, and good performance with a 5.5% power conversion efficiency in larger area (1.0 cm^2) polymer-PCBM solar cells tested in air.[135]

Previously unexplored conjugated polymer architectures incorporating azaheterocycles (see Figure 4) also received increased attention. Although the certain repeat units, such as carbazole or benzothiadiazole were known, the specific combinations, such as those depicted in Figure 4, were not. One such copolymer incorporating known azaheterocycles is PCDTBT (Figure 4) developed by Leclerc et al. At the time, this polymer provided an exciting future for OPV applications, since it has a relatively straightforward synthesis and provides good performance in polymer-PCBM solar cells. In its initial report, the solar cell was fabricated and tested in air providing an efficiency of 3.6%[136], and the device was then further optimized to provide an efficiency of 6.1%.[100,136,137]With a HOMO at -5.45 eV, the polymer is below the threshold for oxidation by ambient O_2 (-5.26 eV), and it is possesses a good hole mobility (1×10^{-3} cm^2 V^{-1} s^{-1}). Another copolymer incorporating an azaheterocycle, quinoxaline, is shown in Figure 4 with TQ1. TQ1 is, again, a synthetically straightforward polymer to prepare, using only thiophene as the donor unit, and provides a power conversion of 6% when blended with PCBM.[138] The final azaheterocycle shown in Figure 4, benzotriazole, is depicted with the copolymer P(BTz-F).[139] Although this particular polymer was studied for its photoluminescence properties, the benzotriazole unit and its analogs have allowed for the development of high-performing, wide band-gap polymers for OPV applications, which are further discussed below. Benzotriazole, as with the other azaheterocycles discussed here, can be synthesized in a few steps. Simple variation of the alkyl chain allows, e.g. linear or branched, allows for the facile tuning of the polymer's properties.

4.2 Polymerization Methods from 2000-2010



Scheme 1. Development of improved conditions for DArP (left), KTCP/GRIM polymerization (right), and SCTP (bottom).

While there were many important advancements relating to conjugated polymer synthesis during the decade of 2000-2010, the significant contributions discussed here include the improvement of conditions for DArP, Kumada catalyst transfer polymerization (KCTP/GRIM), and Suzuki catalyst transfer polymerization (SCTP) (Scheme 1), allowing for the realization of conjugated polymers synthesized using C-H activation and using controlled and living polymerizations, respectively. For DArP, the pioneering work of Ozawa built upon the original conditions described by Lemaire (Figure 3B). It detailed the optimization of the polymerization conditions with the fine tuning of the palladium source and the ligand (Scheme 1).[140] This allowed for the streamlined synthesis of P3AT, and avoided the hazardous and toxic reagents associated with installing the main-group intermediate necessary to promote transmetalation to the active catalyst required for Stille or Suzuki polymerizations.

The discovery of controlled polymerization methods for the synthesis of conjugated polymers was a crucial development for affording defect free conjugated polymers allowing for improved device performance and for polymers with finely tuned architectures.[141–144] For example, in OFET applications having highly regioregular P3HT with low dispersity (Đ < 1.5) can allow for improved mobilities, improving values from 10^{-5}-10^{-4} to 10^{-1}-10^{-2} $cm^2\ V^{-1}\ s^{-1}$, due to high structural order and self-assembly within films.[110,145,146] Methods for the controlled synthesis of conjugated polymers at this time included KCTP, which has an identical polymerization mechanism to GRIM polymerization but can be initiated externally using a transition metal catalyst, and SCTP, which are shown in Scheme 1.[147,148] KTCP/GRIM allowed for the precision synthesis of conjugated polymers with incredibly high structural fidelity, allowing for a variety of architectures, such as homopolymers, polymer brushes, and n-type conjugated polymers.[143,147,149–151] Although the initial report of GRIM for P3AT synthesis was reported just before the start of the 2000-2010 decade, its development thrived through that time, and greater mechanistic insight regarding the polymerization was garnered.[152–155] The seminal work by McCullough described the synthesis of P3AT in good molecular weight (M_n up to 35 kDa) and nearly quantitative rr (Scheme 1). SCTP presented an approachable alternative to KTCP, since it employs the less reactive boronic acid or boronic ester for transmetalation, but many reports during the initial development of SCTP were on simple arene monomers, such as phenylene or fluorene.[156,157] Each of the aforementioned polymerization methods would lead to intensive study regarding the synthesis of conjugated polymers using C-H activation (DArP) or controlled and living polymerization methods (KTCP/GRIM and SCTP).

5. 2010-Present: Extraordinary Polymers through Meticulous Design

From the work of the previous decade (2000-2010), which was dominated by developing new conjugated polymers for OPV applications, many advancements were achieved through the development and application of organic synthetic methods to fine tune the polymer structure. Shown in Figure 5, polymer architectures display much more structurally and synthetically complex architectures when compared to the previous decade, such as new fused ring structures and various heterocycles or heteroatoms. Certain trends for this decade were altered from the previous to suit the developments in device applications, although much work was still intensely focused on OPV applications. For example, rather than the pursuit of narrow bandgap polymers a defining point of this decade was the pursuit of wide bandgap polymers. The use of weak electron acceptor units was explored in order to limit the quinoidal character that is characteristic of many narrow bandgap copolymers. This shift in focus relates to the development of non-fullerene acceptors (NFA), and tuning the absorption properties of the polymer to be complimentary to that of the NFA.[158–162] Additionally, with the advent of the ternary solar cell polymer architectures were adjusted to develop complimentary absorbers and miscible polymer pairs.[163–165] From the tidal wave of synthetic transformations to create new, structurally complex polymers, a trend to target structurally simple conjugated polymers that still exhibit good performance in device applications is developing, which is discussed below.

5.1. Application Driven Design: Conjugated Polymer Structure from 2010-Present for OPV and Emerging Applications t

Shown in Figure 5, azaheterocycles such as pyridine and thiazole replaced thiophene to flank the amide-acceptor DPP, depicted with the polymers PDBPyBT and PDPP2TzT, respectively. These helped to improve the electron affinity of the polymers through reduction in the LUMO energy level, and alleviated steric-hindrance along the polymer backbone allowing for a more coplanar structure, which led to improved performance in either OPV or OFET devices. For

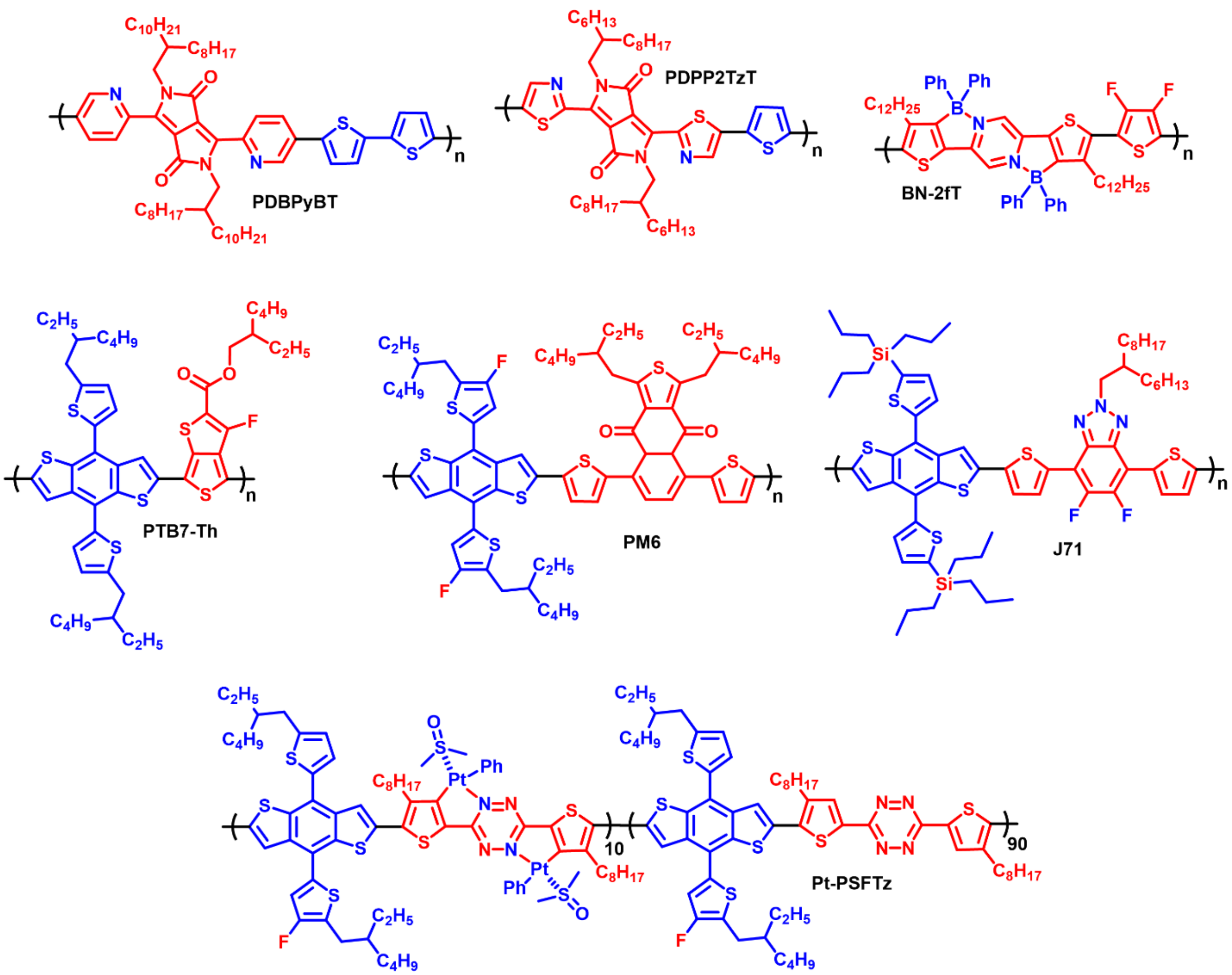


Figure 5. Current conjugated polymer architectures include the creative addition of various heterocycles, coordinating main-group elements, such as boron, 2D-conjugation, the judicious inclusion of halogens or other heteroatoms, and transition-metal coordination polymers

example, PDBPyBT exhibits high hole and electron mobilities, at 2.78 and 6.30 cm^2 V^{-1} s^1, respectively, with a relatively simple copolymer structure.[166] PDPP2TzT was blended into polymer solar cells with PCBM and it provided a power conversion efficiency of just 1.1%, but with further optimization of the donor unit of the copolymer efficiencies of 5.6% could be obtained using this thiazole-DPP acceptor.[167] A more recently applied strategy to induce planarity along the conjugated backbone and thereby improve orbital overlap of the π-system is through Lewis pair and coordination chemistry (with BN-2fT as an example shown in Figure 5).[168] This polymer has diphenyl boron affixed to the polymer, which forms an adduct between the Lewis acid, boron, and the Lewis base, the nitrogen of the pyrazine ring. This makes a highly planar, fused ring system analogous to the fused-ring systems used in many non-fullerene acceptors, and this polymer provides power conversion efficiencies of 8.78% in all-polymer solar cells.[169]

Shown in the polymers PTB7-Th, PM6, and J71 (Figure 5), functionalized benzo[1,2-b:4,5-b']dithiophene has become a near ubiquitous structural motif for top-performing polymers in solar cell applications.[162,170] These polymers exhibit efficiencies extending well above 10% when blended with fullerene or non-fullerene acceptors.[171–175] From comparing these structures from those in Figures 2-4, it is apparent that the synthetic complexity and judicious functionalization of conjugated polymers has increased substantially. The inclusion of the functionalized thienyl unit on the BDT donor provides a 2D-conjugated polymer, and this additional dimension of conjugation allows for improved interactions between polymer chains. This 2D-extension of π-conjugation improves structural order and charge transport.[176,177] The selective fluorination of these polymers is also an interesting structural modification, and a trend developed within the last decade for lowering HOMO energy levels, adjusting the extent of aggregate formation, and tuning the semi-crystallinity.[178–180] To further highlight the synthetic complexity associated with current conjugated polymers, an example that incorporates all of the aforementioned strategies for structural tuning, e.g. fluorination, benzo[1,2-b:4,5-b']dithiophene substituted with 2-alkylthiophenes, and coordination chemistry to facilitate planarity along the conjugated backbone, is Pt-PSFTz. This polymer, although structurally complex, provides notably high efficiencies of 16.5% in polymer-NFA solar cells.[181]

Not all conjugated polymers reported within the last decade are monumental synthetic undertakings, however, with examples shown in Figure 6 of relatively structurally simplistic

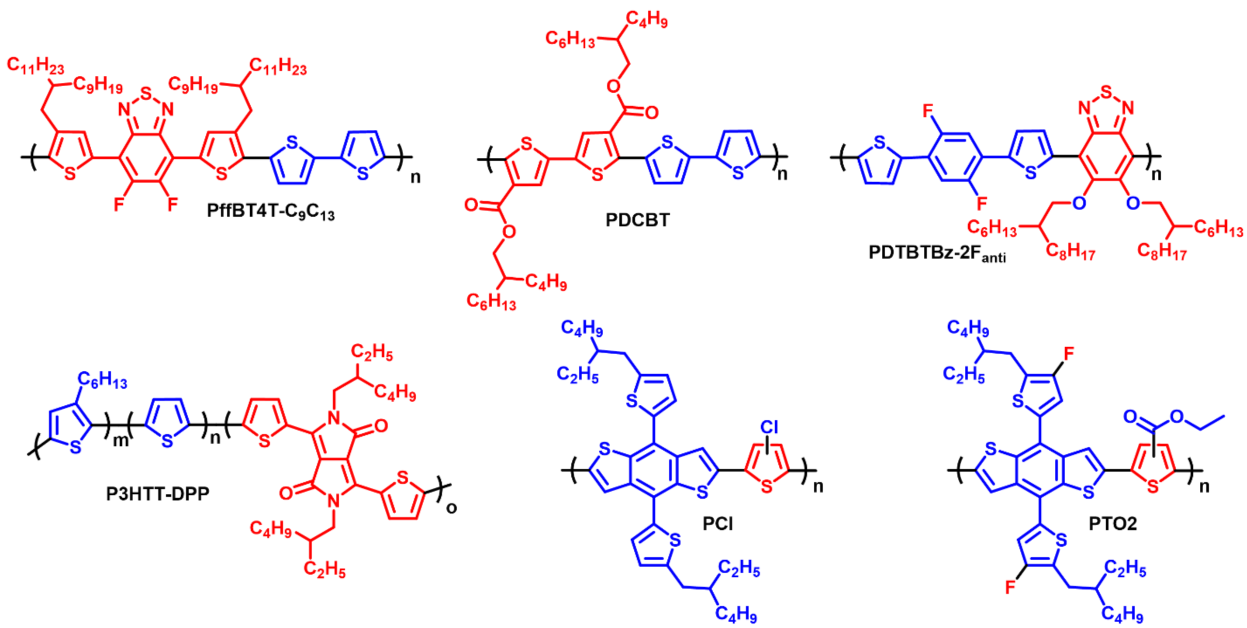


Figure 6. Structurally simpler conjugated copolymers with either streamlined synthetic pathways due to a few number of synthetic steps or the use of simple arenes and heteroarenes for the donor or acceptor units.

conjugated polymers.[182] Polymers such as PffBT4T-C_9C_{13}, PDCBT, and PDTBTBz-$2F_{anti}$ incorporate the commercially available bithiophene donor or a synthetically simple structural analog, and require only a few synthetic steps for their complete synthesis. These polymers still provide good efficiencies in polymer solar cells with values of 11,7%, 10.2%, and 9.8%, respectively.[183–186] As alluded to in this perspective, scaling back the number of synthetic steps for monomer synthesis also alleviates the added cost associated with conjugated polymer preparation since numerous synthetic and purification steps are avoided. This lowers cost by avoiding materials and reagents associated with reaction setup, workup, and purification. Additionally, the waste associated with each of these processes is also minimized, which also addresses environmental concerns.

In addition to these, structures such as semi-random polymers or terpolymers, such as P3HTT-DPP in Figure 6, provide a simplistic means to tuning the polymer properties. This is accomplished through the strategic incorporation of simple conjugated repeat units where composition and sequence distribution of the repeat units are used to tune the polymer properties, which is further elaborated upon below.[187–191] In comparison to the polymers shown in Figure 5 with heightened structural complexity, benzo[1,2-b:4,5-b']dithiophene based copolymers with structurally simple acceptor units, shown in Figure 6 with PCl and PTO2, can still provide desirable performance with efficiencies of 12.1% and 14.7% in polymer solar cells, respectively.[192,193]

Aside from the meticulous modification of monomer structure to alter the corresponding electronic and physical properties of the polymer, an often simpler, approachable, and effective strategy is to synthesize a terpolymer, where a third monomer is incorporated into the polymerization. Extensive reviews discussing specific design strategies and architectures have been published, and so the reader is directed to those for further elaboration on the subject.[188,194,195] Overall, this strategy allows for broadening the absorption, adjusting the aggregation, and modifying the semi-crystallinity of the polymer, and for these reasons terpolymers have been largely incorporated into OPV device applications as donor or acceptor materials. For donor-acceptor copolymers, the terpolymer analog could incorporate two donors to form a two donor, one acceptor (2D1A) architecture, or two acceptors and 1 donor to form a one donor, two acceptor (1D2A) architecture. Examples of terpolymers are depicted in Figure 7 and discussed below.

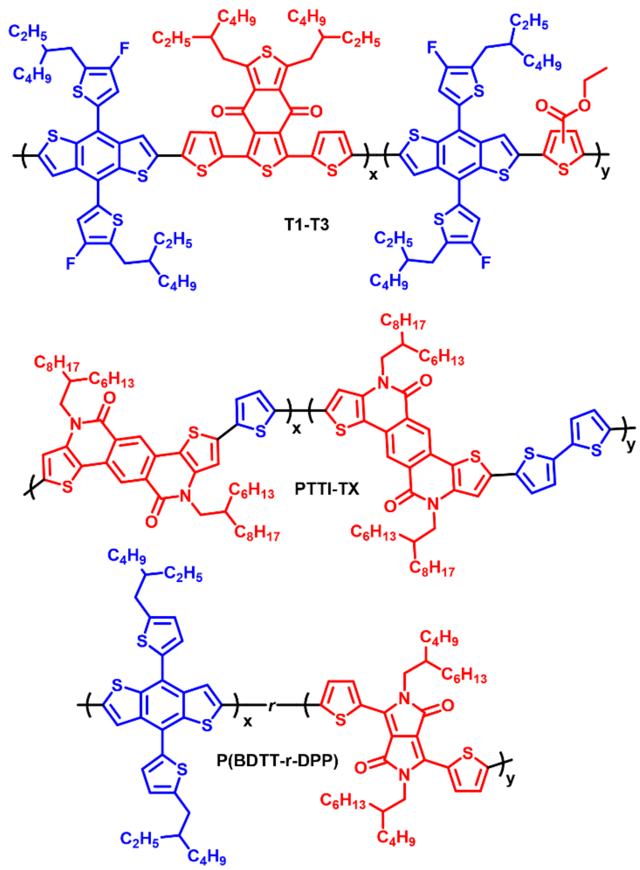


Figure 7. Examples of the various architectures possible with terpolymers including 1D2A (T1-T3), 2D1A (PTTI-TX), and random (P(BDTT-r-DPP). An example of semi-random is shown in Figure 6 with P3HTT-DPP.

The terpolymers T1-T3, where the amount of the ester-thiophene acceptor is varied, is an excellent example of a 1D2A terpolymer (Figure 7).[196] The strategy for these polymers was to broaden the absorption profile to allow for extended absorption from 500 to 700 nm. When blended with the NFA, IT-4F, efficiencies for the polymer solar cells reached as high as 15.1%. Additionally, encapsulated blade coated devices showed improved stability relative to the ternary blends composed of the respective homopolymers (PBDB-T and PT02) providing a clear example of the advantages of terpolymers. PTTI-TX (Figure 7) is an example of a 2D1A terpolymer incorporating varying degrees of the simple donor units thiophene and bithiophene.[189] By varying the quantity of bithiophene present the morphological and charge transport properties were able to be optimized to afford polymer solar cells with efficiencies up to 10.8% when using PCBM as the acceptor. A final example of a terpolymer is shown with P(BDTT-*r*-DPP) (Figure 7), which does not fit into the classification of either 1D2A or 2D1A but is a random copolymer.[197] With this polymer, the composition of the backbone is tuned to allow for donor-donor or acceptor-acceptor homocouplings in addition to the more common donor-acceptor coupling. This broadens the potential for various linkages to be obtained, and allowed for extended absorption from the UV to near-IR regions. Efficiencies up to 5.63% were obtained in polymer-PCBM solar cells using this particular synthetic strategy.

5.2 Polymerization Methods from 2010-Present

Although research in the area of controlled or living polymerization for the synthesis of conjugated polymers remains ongoing, an intense area of current study is with DArP. DArP provides a sustainable method for conjugated polymer synthesis, and it can be used for a variety of architectures, such as homopolymers, donor-acceptor copolymers, and terpolymers.[198–201] Sustainability with DArP is enhanced compared to other transition metal catalyzed polymerization methods, because it does not require installation of boronic acid/ester or trialkylstannane for transmetalation, which significantly lowers the environmental impact associated with monomer and polymer synthesis. Specifically, the amount of waste, such as the toxic tin waste associated with Stille polymerization, is reduced, and the reagents associated with monomer functionalization are reduced. While certain polymerization methods, such employment of the Wittig reaction for polymerization, do not require toxic tin reagents or a transition-metal catalyst, these methods do not have a low atom-economy, require numerous steps to install the reactive functionalities for the polymerization, and can be limited in scope in comparison to DArP. Emerging polymerization methods for the preparation of conjugated polymers in the current decade are mostly based on the pioneering studies by Lemaire and Ozawa, which were previously discussed and described conditions for the synthesis of P3HT using C-H activation.[98,140] Many reviews discussing the recent developments for DArP are available, and so the reader is directed to those for deeper insight, but general conditions for DArP are provided in Scheme 2.[198–200,202,203] Examples of polymer structures from these pioneering studies are provided in Figure 8A with P3HT and PDOF-TP from the works of Ozawa et al. and PDOF-BTz and PBTTPD from Kanbara et al. and Leclerc et al., respectively.[140,204–206] It should be noted, that the development of DArP was reliant on the pioneering small-molecule C-H activation studies by Fagnou et al.[207–211] Even

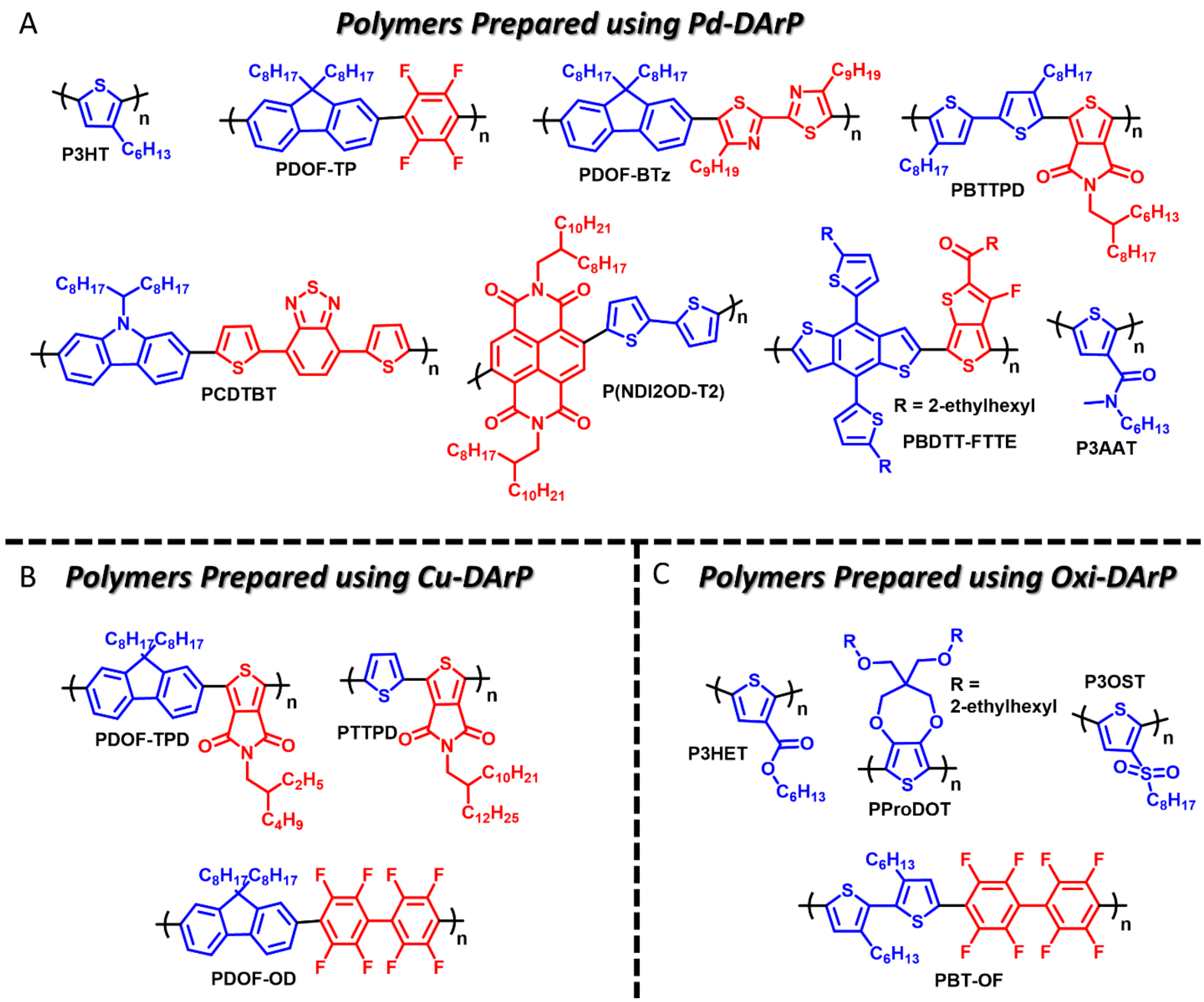


Figure 8. (A) Examples of conjugated polymers prepared using Pd-catalyzed DArP. (B) Examples of conjugsted polymers prepared using Cu-catalyzed DArP. (C) Examples of conjugated polymers prepared using Oxi-DArP.

though DArP had been demonstrated in 1999 by Lemaire (Figure 3), the small-molecule studies of Fagnou et al. provided mechanistic insight and strategies to improve the polymerization outcome, such as the inclusion of a carboxylic acid additive.[210]

From these initial studies, conditions were disclosed that allowed for the preparation of polymers with much greater structural complexity and more relevance for device applications, such as PDCBT, P(NDIOD-T2), and PBDTT-FTTE (Figure 8A).[212–214] Although not depicted in

Figure 8, our group and others have demonstrated convergence in PCE for a variety of polymers prepared using DArP when compared to their Stille or Suzuki counterparts in polymer solar cells.[213,215–217] It has also allowed for the streamlined synthesis of new polymer architectures, such as P3AAT in Figure 8, which can be solution processed in the sustainable solvent, n-butanol.[218] Although the field of Pd-DArP has made momentous strides since Lemaire's original report, much remains to be done. For example, while condition sets can be applied to monomers with similar structure, often extensive optimization must be done for each new set of monomers due to the inherent differences in C-H bond reactivity. Additionally, much of the Pd-DArP describes the activation of C-H bonds on thiophene and its analogs, but conditions describing the C-H activation of other heteroarenes and arenes remain sparse in comparison.

To further enhance the sustainable aspects of DArP, we have recently reported conditions that allow for the synthesis of conjugated polymers using a Cu-catalyst in place of Pd.[219–221] Examples of polymer structures prepared using Cu-DArP are depicted in Figure 8B, with PDOF-TPD, PTTPD, and PDOF-OD. Given the recent disclosure of conditions allowing for the preparation of polymers using Cu-DArP, much work has to be done with expanding this methodology to a broader scope of monomers and evaluating the polymer products in device applications.

In addition to Cu-DArP, another emerging method for conjugated polymer synthesis is Oxi-DArP, for which general conditions are provided in Scheme 2.[222–224] This presents a highly sustainable pathway for conjugated polymer synthesis, since it proceeds through dehydrogenative coupling, and the reader is directed to a recent review highlighting work in both Pd and Cu-catalyzed Oxi-DArP.[201] In brief, Oxi-DArP requires the addition of an oxidant to the polymerization in order to oxidize the catalyst to its active species, and it proceeds without the need of functionalizing the monomers, such as with a halogen. As with Cu-DArP, Oxi-DArP is still an emerging method for polymerization. Examples for polymers using this methodology are shown in Figure 8C with P3HET, PProDOT, P3OST, and PBT-OF.[222,223,225–227]

It should be clear from a cursory glance over Figures 1 through 6 how the structure of conjugated polymers evolved throughout the decades from their initial period of focus in the 1970s-1990. The judicious modification and inclusion of various functionalities have allowed for the tailoring of conjugated polymers to provide high-performance in a variety of applications. Likewise, methods for their synthesis evolved from polymerizations that required numerous steps to install the reactive functional groups, such as Wessling or Wittig polymerization, or that resulted in low selectivity and poor structural fidelity, such as chemical and electrochemical oxidative polymerizations. These polymerizations have now been replaced with those allowing for the controlled polymerization, e.g. KTCP/GRIM and SCTP, or those that proceed through C-H activation, e.g. DArP and Oxi-DArP. There are still many areas within the field of conjugated polymers that have opportunities for exciting new developments. While the polymers discussed in this perspective mostly applied to OLED, OFET, and OPV applications, areas such as bioelectronics, stretchable or deformable electronics, light driven photocatalysis, and metallo-polymers are also rapidly evolving and offer many areas for new development.[228–231] Moving forward, the field of conjugated polymers is now at a point where the lingering synthetic issues are how to design a polymer that provides suitable performance without significant synthetic complexity, and further developing more sustainable conditions for DArP and Oxi-DArP which enable the synthesis of polymers through C-H activation.

6. The Present Decade: Identifying New Polymers to Address Current Challenges

From the intensive research regarding the structure-function properties of conjugated polymers, numerous synthetic strategies have been introduced to allow for the tailoring of various conjugated polymer structures and architectures. Moving forward into the next decade, the following section presents emerging areas for conjugated polymer design. Also, as mentioned throughout, the structural complexity has challenged the fundamental idea that conjugated polymers can alleviate issues associated with material cost when compared to their inorganic counterparts; however, an often-overlooked issue is conjugated polymer stability. Often, high-performing conjugated polymers are not also studied for their stability under ambient conditions. Frequently, stability tests, such as thermal or light stability, are conducted under inert atmosphere void of the atmospheric oxygen that destroys the structural integrity of conjugated polymers. Given the impending commercialization of many organic electronic technologies, concern regarding conjugated polymer stability has increased, and strategies to improve that are presented. In addition, synthetic strategies to develop more flexible and deformable conjugated polymers are also presented. This highlights the movement of conjugated polymer electronic devices from the small-scale laboratory setting where devices are typically fabricated using glass substrate to a commercial setting where large-scale fabrication occurs on flexible substrates. Another emerging area of conjugated polymer design discussed is single-component polymer solar cells (SCPSC). These polymers seek to revolutionize the field of OPV by eliminating the need for a binary system, in which a polymer donor and polymer or small-molecule (PCBM or NFA) acceptor are employed, to a single component where the donor and acceptor are covalently linked. This simplifies the device fabrication process, since only a single component is required for the formulation of the active layer rather than multiple, individual components. Also, covalently linkage of the donor and acceptor may help to alleviate phase-segregation of the donor and acceptor allowing for a more stable bicontinuous morphology, which is critical for prolonged use. Importantly, conjugated polymer structures for mixed ion conductors where the polymer serves to transport charge and mass are presented, which is a relatively emerging application for conjugated polymers. This section details the design of polymers in organic electrochemical transistors (OECT), batteries, light-emitting electrochemical cells (LEEC), and bioelectronics. Lastly, this section concludes with applications for conjugated polymers outside of conventional organic electronic devices, e.g. OPV, OLED, and OFET. The topics include polymers for visible light photocatalysis and biological imaging, sensing, and therapeutics.

In terms of the historical underpinnings for the design and synthesis of new conjugated polymer architectures, much of the work completed during the time-period of 2000-2020 provides the greatest insight with how structure modulates function, which is of course built upon that of the previous decades, and the emergent synthetic tools for designing and preparing new polymers. Often, polymer architecture changes with the trends or developments for a given area of research. For example, the development of donor-acceptor copolymers from narrow bandgap (2000-2010) to wide bandgap (2010-2020) to better compliment the absorption properties of NFAs rather than PCBM. Moving forward, it remains to be seen how the design and integration of donor and acceptor units will be integrated into novel macromolecular assemblies for some of the applications described below. However, the improved understanding of how structure modulates the electronic properties and function, such as donor-acceptor pairing, side-chain engineering, and heteroatom modification, allows for a broad but relatively defined palate to fill in the blank canvas.

6.1 Application Driven Design: Addressing How Conjugated Polymer Stability can be Improved in Device Applications

A critical issue that must be addressed for commercialization of conjugated polymer electronic devices is material stability.[232–234] Many conjugated polymer materials are inherently unstable

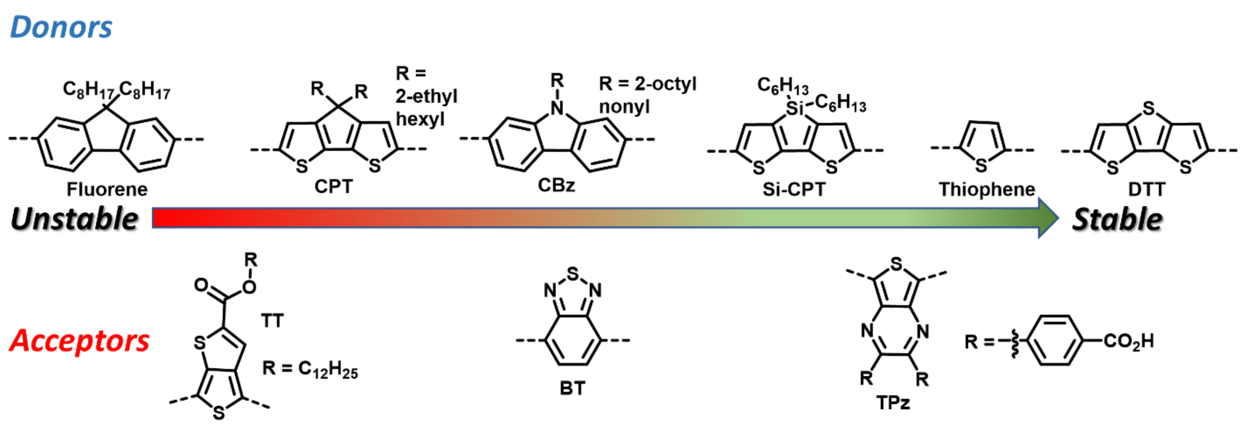


Figure 9. A qualitative depiction of the relative resistance to photochemically induced oxidative decomposition of commonly used donor and acceptor units. It should be noted that this figure is not to scale and compares only donors or acceptors respectively with each other.

under conditions encountered in a typical environment, which has uncontrollable temperature, humidity levels, and constant exposure to atmospheric O_2. Studies by Manceau et al. using P3HT have shown that photo- and thermo-oxidation causes radical induced oxidation of the n-hexyl sidechains leading to degradation of the polymer. The reactive radical species initiated from the oxidation of the side-chains can further oxidize the conjugated backbone of the polymer, such as the sulfur of the thiophene leading to sulfones and ultimately sulfonate esters, decimating the structural integrity of the conjugated polymer.[235,236] Another study by Stingelin and Troshin et al. of over twenty polymers, including PPV and PCDTBT, shows polymer degradation can also be attributed to photochemical crosslinking.[237] While encapsulation techniques can protect the conjugated polymer from direct contact with the outside environment, these can raise the costs of device fabrication and if a glass-encapsulent is used it can prohibit the application towards flexible devices. Strategies for improving device stability are an important topic, but will not be addressed here since the focus of this discussion is on designing more robust conjugated polymers, and so the reader is directed to relevant reviews and articles.[238–242] To address this problem directly, evaluating the monomers for their propensity to degrade and selecting more stable monomers may improve the environmental stability of conjugated polymers. As shown in Figure 9 and based on a study by Krebs et al., the use of donor and acceptor units without side-chains promotes polymer stability through resistance to photochemically induced oxidative decomposition. For example, donor units with alkyl substituents, such as fluorene, are much more unstable than those without, such as thiophene and DTT.[232,233] However, alkyl substituents profoundly influence the physical properties of polymers, such solubility and crystallinity, and so developing robust, high-performance polymers is not as simple as removing the alkyl substituents.

Interestingly, some conjugated polymers have been shown to have excellent resistance to oxidation, such as PBDTTPD (Figure 4). In a study by Leclerc et al., this polymer was shown to be highly resistant to oxidation, providing little to no change in absorbance up to 200 hours. This stability was attributed to the chelation or antioxidant effects of intermediate degradation products, which interrupted and slowed the rate of oxidative decomposition.[243] Conversely, polymers such as PTB7-Th (Figure 5) have been shown to have almost completely quenched absorption due to oxidation of the polymer after only 20 hours.[244]

More specific to OPV applications, a study by McCulloch et al. detailed the argument that polymer donors were designed to have their HOMO and LUMO energy levels optimized for blending with PCBM in order to obtain a high V_{OC}, and that the high LUMO energies of many polymers could lead to the degradation of polymer and acceptor blends through the generation of superoxide from photo-oxidation.[245] They make the important point that with the advent of NFA acceptors, which can be tailored to afford a wide-range of HOMO and LUMO energy levels, conjugated polymers with reduced LUMO energy levels could be designed allowing for improved material stability and extended device performance. This presents some challenges, however, since the HOMO and LUMO of the polymer must be tuned concertedly with that of the NFA to allow for facile charge transfer, and the bandgap of the polymer should still allow for facile light absorption in the visible region.

6.2 Developing New Polymer Architectures for Flexible and Transient Electronics

Since a desired application for conjugated polymers is in flexible devices, developing conjugated polymers (which are typically brittle and become damaged irreversibly after repeated deformation) that are inherently stretchable and flexible has become a recent focus.[230,246–249] A strategy introduced by Sivula et al. and further developed upon by Mei et al. to develop more flexible electronics was to introduce conjugated break spacers (CBS) into the backbone, which is depicted with the polymers PBTTT-C14-*co*-DBT, TEG-DPP-C5, and Si-DPP-C5 (Figure 10).[250–252] It can be seen that a C10 or a C5 saturated linker is placed between the two thienyl units of these polymers, respectively, imparting potential flexibility and deformability in device applications. For PBTTT -C14-*co*-DBT (Figure 10), it was found to provide a hole mobility (μ_h) of 0.01 cm^2 V^{-1} s^{-1} in an OFET device, which decreased to 4 × 10^{-4} cm^2 V^{-1} s^{-1} after thermal annealing.[251] The value for hole mobility is lower than that reported for PBTTT-C$_{14}$ in the report by McCulloch et al. discussed above (0.2-0.6 cm^2 V^{-1} s^{-1}), but is still relatively high when compared to many other conjugated polymers.[109] While PBTT-C14-*co*-DBT had the architecture of a block copolymer, Mei et al. found even with complete incorporation of the break spacer the field-effect mobility for TEG-DPP-C5 and Si-DPP-C5 (Figure 10) was 2.1 × 10^{-4} cm^2 V^{-1} s^{-1} and 3.4 × 10^{-3} cm^2 V^{-1} s^{-1}. The siloxane terminated side-chains could provide shorter π-π stacking distances between chains, and this study serves as a good example of conjugated polymer side-chain engineering.[60,252,253] While the mechanical properties of these particular polymers were not

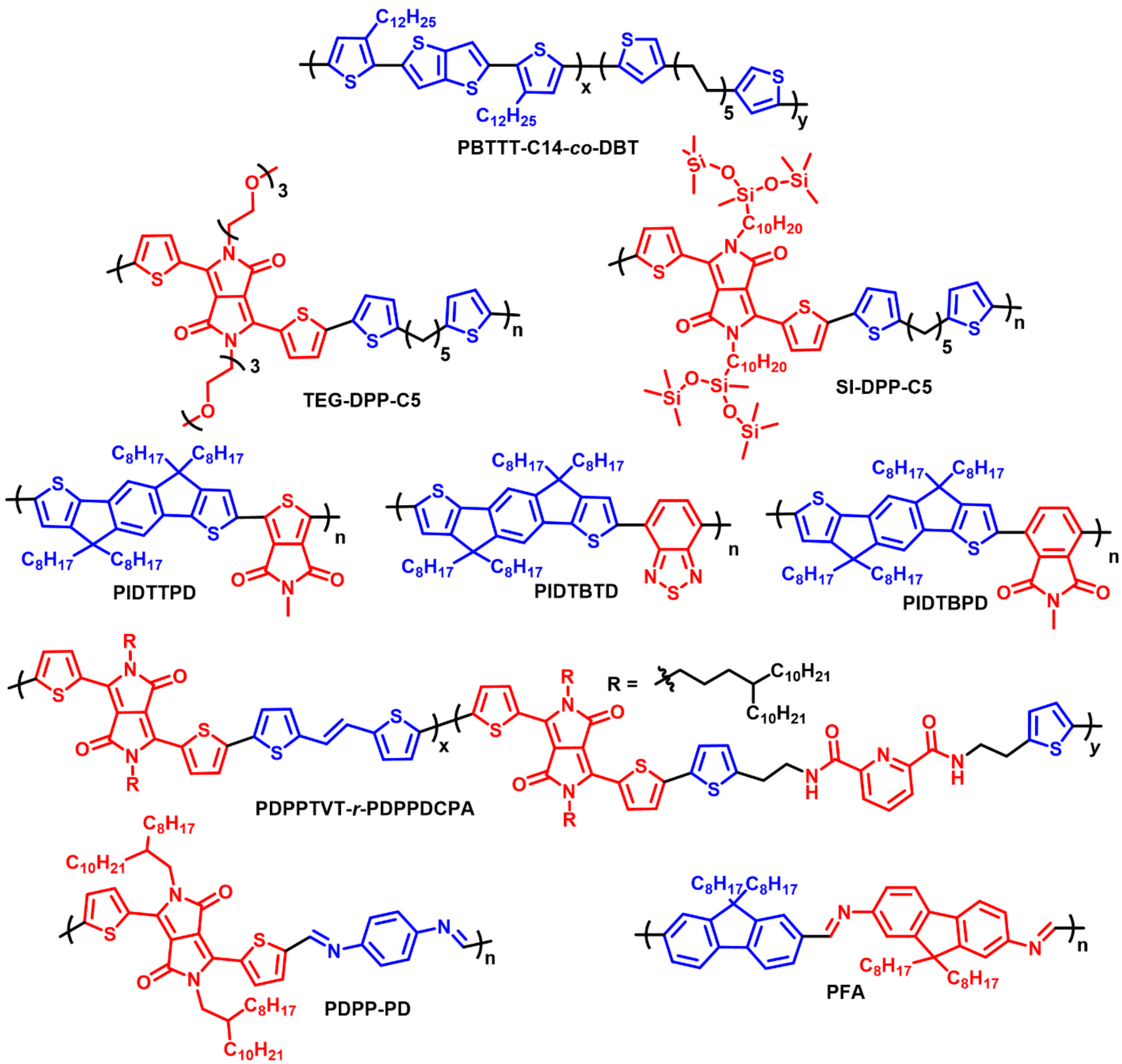


Figure 10. Examples of emerging conjugated polymer architectures for flexible electronics (TEG-DPP-C5 to PDPPTVT-*r*-PDPPDCPA) and transient electronics (PDPP-PD and PFA).

investigated, polymers of similar structure and CBS polymers with varying structures, such as semi-random or terpolymer architectures, have been studied.[231,254] A strategy by Luscombe et al. was to use the steric hindrance imposed by the alkyl substituents in the indacenodithiophene unit of the polymers PIDTTPD, PIDTBTD, and PIDTBPD (Figure 10) where the weak intermolecular interactions between polymer chains allowed for a low elastic modulus and high ductility without comprising the field-effect mobilities of 0.06 to 0.20 $cm^2\ V^{-1}\ s^{-1}$. Aside from integrating aliphatic carbon chains into the backbone of the polymer other units can be incorporated, such as 2,6-pyridine dicarboxamide (PDCA), which is depicted in Figure 10 with PDPPTCT-*r*-PDPPDCPA reported by Bao et al.[246] Following the CBS-strategy developed by Mei et al., integration of the PDCA unit into the backbone allows for hydrogen bonding between polymer chains. The network of hydrogen bonds allows for recovery of the native morphology, through solvent vapor and thermal annealing after stress or strain has been introduced, while maintaining an average field-effect mobility of over 1 $cm^2\ V^{-1}\ s^{-1}$. This value for mobility is similar to that of the polymer without any PDCA which had a field-effect mobility of just under 1 $cm^2\ V^{-1}\ s^{-1}$. Applying these architectures to high efficiency OPV devices, which currently have record efficiencies approaching 18%, remains a challenge and an area for future work.[255]

Another emerging architecture is the use of an imine linker, also referred to as polyazomethines, polyimines, or Schiff-base conjugated polymers, with PDPP-DP and PFA as examples in Figure 10. Although these polymers have been known for decades with an initial study by Jenekhe et al. and numerous studies by Skene et al., interest in these architectures has reemerged due to their potential application in transient and bioresorbable electronics.[256–265] While bioresorbable small molecules, such as indigo and carotenoid polyenes, have been integrated into OFET devices, application of conjugated polymers remains limited with PDPP-PD being the only example where device degradation was investigated, to our knowledge.[266] In this study, Bao et al. observed that PDPP-PD provided field-effect mobilities up to 0.34 $cm^2\ V^{-1}\ s^{-1}$. While imine linkages require an acid catalyst for degradation, it is surmised that degradation can occur in the stomach, and with the addition of more hydrophilic substituents and linkers more susceptible to hydrolysis at a neutral pH conjugated polymers that can degrade in a more general setting may be realized.

6.3 Single-Component Organic Photovoltaics

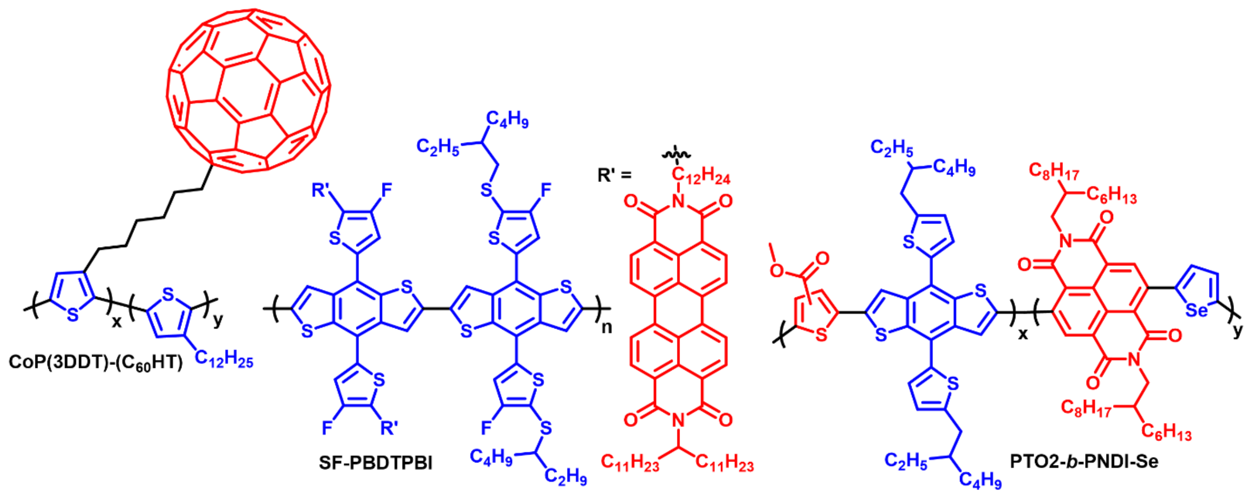


Figure 11. Examples of conjugated polymer architectures used for single-component polymer solar cells (SCPSC).

An emerging area for OPV that requires the design and synthesis of new conjugated polymer architectures is single-component polymer solar cells (SCPSC) (with examples shown in Figure 11).[267] While the concept of SCPSCs is not new and the devices typically provide lower PCEs compared to their binary, bulk-heterojunction counterparts, the potential for this technology to simplify device the device fabrication process and provide a more stable morphology make this an area of expanding interest.[268–270] Pierini et al. demonstrated an excellent efficiency of 5.58% with CoP(3DDT)-(C_{60}HT) (Figure 11), using an active layer composed of electrospun fibers.[271] While solution processed films of CoP(3DDT)-(C_{60}HT) provided efficiencies of 2.43% in OPV devices, the nanofibers prepared from electrospinning provided improved structural order and π-π stacking between polymer chains allowing for improved efficiency. The double-cable polymer SF-PBDTPBI (Figure 11) was developed through structural optimization, e.g. inclusion of the fluorine and sulfur heteroatoms, and provides an example of a perfectly alternating donor-acceptor copolymer where the PDI acceptor is tethered or attached to the polymer backbone via an aliphatic cable. This well-defined copolymer architecture allowed for nanophase-separation forming an ideal morphology for charge transport, and it provided an efficiency of 4.18%.[272] Another architecture, which does not invoke this use of a tethered or cabled acceptor, is the block copolymer PTO2-*b*-PNDI-Se (Figure 11).[273] The block copolymer architecture allows for nanophase separation and the formation of well-defined domains of the donor and acceptor, as with the aforementioned double-cable architecture. This strategy provided an efficiency of 3.87%, which is a significant improvement when compared to the efficiency of 1.14% achieved by the binary all-polymer solar cell composed of the two separate, respective polymers that make up the block copolymer, PTO2 and PNDI-Se.

6.4 Mixed Ion Conductors

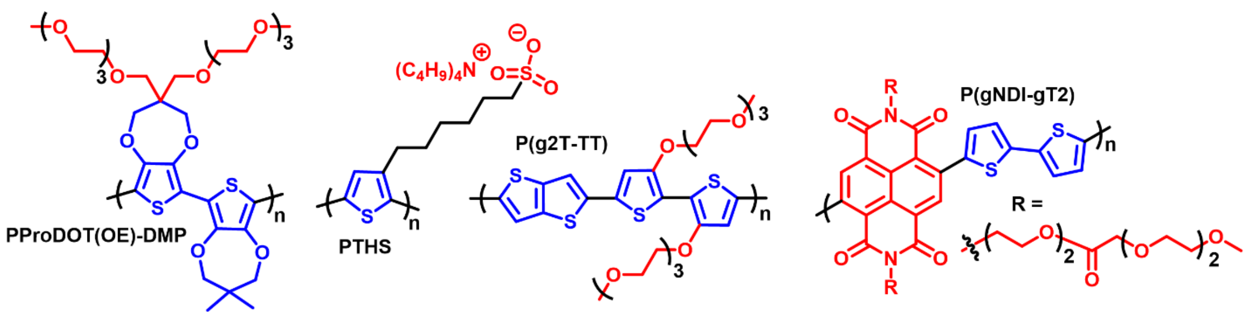


Figure 12. Examples of conjugated polymer structures used for mixed ion conduction applications.

Mixed ion and charge transport applications, such as in organic electrochemical transistors (OECT), batteries, light-emitting electrochemical cells (LEEC), and bioelectronics provides another area for future growth and expansion in the field of conjugated polymers.[274–280] In such applications the conjugated polymer serves to transport charge and mass, in the form of ions, and the conjugated polymers typically used for these purposes are designed through the integration of components that are known to transport charge well. For charge transport a coplanar conjugated backbone with extensive π-π interactions is preferred, and for mass side-chains that can coordinate to a mobile ion to facilitate its transport are used (with examples shown in Figure 12). In a study by Reynolds et al., PProDOT(OE)-DMP (Figure 12) was designed to possess good hydrophilicity with the oligo-ether substituents, and the dimethyl functionalized ProDOT was included to reduce steric hindrance along the conjugated backbone.[281] The polymer was investigated for its charge storage properties, and a gravimetric capacitance exceeding 80 F g^{-1} was observed. PTHS (Figure 12), a simple P3HT analog with a sulfonate at the end of the alkyl substituent (akin to P3-ETSNa in Figure 2), was evaluated for its performance in OECT devices operating in accumulation mode by Malliaras et al., and it was found to have a high transconductance when ethylene glycol was used as a cosolvent.[282] Rivnay and McCulloch et al. developed a PBTTT analog with oligoethylene glycol substituents, P(g2T-TT), and found that the side-chains likely improve ion penetration and transport allowing for high transconductance in OECT devices.[283]Lastly, McCulloch and Müller et al. found that polar side-chains on an n-type copolymer for thermoelectric applications, P(gNDI-gT2), improves miscibility with the molecular dopant, benzimidazole-bimethylbenzenamine (N-DMBI), affording conductivities of 10^{-1} S cm^{-1} with dopant concentrations of 10 mol%.[284] From the acquisition of knowledge garnered from the previous decades, the emerging areas for conjugated polymer and synthesis demonstrate how structure, either with the repeat units incorporated, or the substituents, such as the choice of alkyl side-chains, can be finely tuned to address new and emerging applications.

6.5 Conjugated Polymers for Other Applications: Photocatalysis and Therapeutic, Sensing, and Imaging Applications

Although this perspective has been focused on the design and synthesis of conjugated polymers pertinent to organic electronic device applications, such as OPV, OLED, and OFET, other important areas of research that deserve recognition include photocatalysis and biological applications, such as imaging, sensing, and therapeutics. The use of conjugated polymers for photocatalysis and biological applications has been done for decades, but the section will highlight more recent work with concluding remarks for future work. Briefly, conjugated polymers designed for photocatalysis applications can be used for water splitting, degradation of persistent organic dyes, the reduction of CO_2 into valuable chemical feedstocks, and the photocatalytic reduction and oxidation (photoredox) reactions of organic small-molecule substrates. An excellent review on the subject has been recently published, and so readers are referred there as well as more general reviews regarding these topics.[229,285–288] Examples of polymers used for photocatalytic water splitting are shown in Figure 13A, including PFOD-TBT, PFBT-CPE, and PBDTBT-7EO, and it can be seen that the conjugated backbone of these polymers incorporates relatively simple repeat units, such as fluorene and benzothiadiazole.[289–291] It should be noted that polymers with other repeat units have been prepared, but these examples were simply chosen to provide brevity for the discussion of this topic. Since water-splitting occurs in aqueous media, hydrophilic polar and ionic side chains, such as the quaternary ammonium salt of PFBT-CPE or the oligoethers of PBDTBT-7EO, allow for the polymers to remain dispersed in solution promoting reactivity. From the earlier work of Yanagida et al., which described the use of PPP (Figure 2A) obtaining a hydrogen evolution rate (HER) of 207.5 μmol h^{-1} g^{-1} under 290 nm light, PFOD-TBT, PFBT-CPE, and PBDTBT-7EO provide often significantly improved rates of 50 mmol h^{-1} g^{-1}, 512 μmol h^{-1} g^{-1}, and 40 μmol h^{-1} g^{-1} under visible light.[289–291] In contrast, Yanagida et al. report that H_2 production was negligible when using PPP under visible light.[292] Much work within the field of photocatalytic reactions using conjugated polymers remains to be done, such as designing

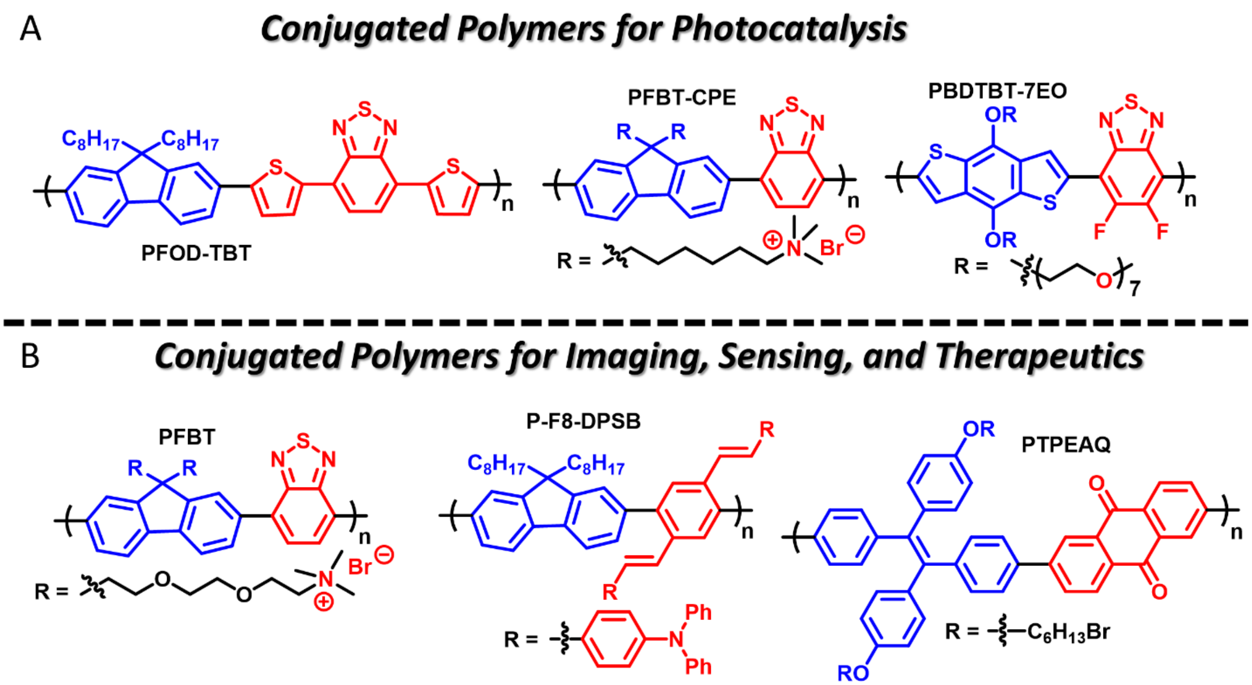


Figure 13. (A) Examples of conjugated polymers for photocatalysis. (B) Examples of conjugated polymers for imaging, sensing, and therapeutics.

polymers that absorb well in the visible region and that can undergo the desired charge transfer for a given catalytic reaction. While the polymers described in this section used the donor-acceptor structural motif to tune the absorption properties and altering the side-chains to increase the hydrophilicity, much can still be done in regards to structural modification to improve performance. Methods for structural modification can be found in the other sections in this perspective, such as tuning FMO energy levels through the installation of various functional groups, side-chain engineering, and heteroatom modification.

Lastly, examples of conjugated polymers used for sensing, imaging, and therapeutic treatment are shown in Figure 13B with PFBT, P-F8-DPSB, and PTPEAQ, respectively.[293–295] Excellent reviews have also been published on these topics, and so the reader is directed there for further insight.[296–299] As an example of biological sensing capabilities, a study by Liu and Bazan et al. disclosed the incorporation of the water soluble PFBT (Figure 13B) into a sensing platform for the detection of single stranded DNA (ssDNA).[294] This polymer again incorporates the simple fluorene and benzothiadiazole repeat units to form a donor-acceptor copolymer. It was found that by including Ag nanoparticles metal enhanced fluorescence (MEF) was observed allowing for the increased detection of the ssDNA. In the case of imaging, Tian et al. described the incorporation of P-F8-DPSB (Figure 13B) and a near-infrared (NIR) light absorbing dye to generate fluorescent nanoparticles.[293] These nanoparticles were used in the imaging of HeLa cells with observable fluorescence through a mock tissue with a thickness of 900 μm after excitation at 650-730 nm. The polymer possesses an interesting structure with a bis(diphenylaminostyryl)benzene chromophore, which allows for multiphoton fluorescence imaging.[300] For therapeutic applications, PTPEAQ was meticulously designed as a donor-acceptor copolymer. Specifically, the tetraphenylthylene (TPE) unit was chosen due to its propensity to undergo aggregated induced emission (AIE).[301,302] The anthroquinone acceptor was selected because it has been previously used to for the preparation of far-red (FR) and NIR dyes that possess a low energy difference between the lowest singlet and triplet excited states (ΔE_{st}) allowing for intersystem crossing (ISC).[303] The PTPEAQ polymer was then used to form nanoparticles that were subsequently functionalized with the HER2 antibody. The desirable photophysical properties of the polymer allowed for efficient $^1O_2$ generation to facilitate the selective death of SKBR3-cancer cells over NIH-3T3 normal cells when the functionalized nanoparticles were illuminated with white light. As with the polymers for photocatalytic applications, there are still areas for improvement with polymers for biological applications. A major hurdle remains in developing efficient absorbers at low-energy wavelengths, such as NIR/NIR-II, allowing for the improved penetration depth of light.

7. Conclusion

An overview for the field of conjugated polymers throughout the decades (1970s-present) and an outlook on emerging areas for conjugated polymer synthesis and design has been provided with a keen focus on important changes in polymer structure and polymerization methods. Specifically, the synthetic transformation and growth of conjugated polymer design from simple repeat units, often only consisting of a single arene or heteroarene, to donor-acceptor copolymers and terpolymers with semi-random or random structures was illustrated. The increase in structural complexity reflects how the inclusion of various transformations from organic synthesis enabled the tailoring of such structures, and how further understanding of the operating principles for a given device application, e.g. OLED or OPV, further inspired the structural tuning of conjugated polymers.

In the early years of the concerted and focused efforts on conjugated and conductive polymers (1970s-1990), fundamental properties were determined using relatively simple structures. In the following decade (1990-2000), improvements in polymer synthesis, such as the application of transition metal catalyzed cross-coupling reactions for polymer synthesis, allowed for polymers with improved structural fidelity and their subsequent characterization in organic electronic devices. This set the stage for the following decades (2000-2020), since new structures could be tested and tailored using the metrics provided from a device application as a source of feedback. Moving forward, the field is now at a point where it can benefit from structural simplicity and work to develop polymer architectures with increased environmental and device stability. Additionally, the sustainable synthesis of conjugated polymers, such as through DArP or Oxi-DArP, has much room for expansion, with the discovery of more sustainable catalysts, such as those based on copper, allowing for the synthesis of various conjugated polymer architectures, including donor-acceptor copolymers.

Corresponding Author

*barrycth@usc.edu

ACKNOWLEDGMENT

This work was supported by the National Science Foundation (MSN under award number CHE-1904650).

REFERENCES

[1] R.R. Søndergaard, M. Hösel, F.C. Krebs, Roll-to-Roll fabrication of large area functional organic materials, J. Polym. Sci. B Polym. Phys. 51 (2013) 16–34. https://doi.org/10.1002/polb.23192.

[2] G. Luo, X. Ren, S. Zhang, H. Wu, W.C.H. Choy, Z. He, Y. Cao, Recent Advances in Organic Photovoltaics: Device Structure and Optical Engineering Optimization on the Nanoscale, Small. 12 (2016) 1547–1571. https://doi.org/10.1002/smll.201502775.

[3] S. Günes, H. Neugebauer, N.S. Sariciftci, Conjugated Polymer-Based Organic Solar Cells, Chemical Reviews. 107 (2007) 1324–1338. https://doi.org/10.1021/cr050149z.

[4] O. Ostroverkhova, Organic Optoelectronic Materials: Mechanisms and Applications, Chem. Rev. 116 (2016) 13279–13412. https://doi.org/10.1021/acs.chemrev.6b00127.

[5] J. Mei, Y. Diao, A.L. Appleton, L. Fang, Z. Bao, Integrated Materials Design of Organic Semiconductors for Field-Effect Transistors, J. Am. Chem. Soc. 135 (2013) 6724–6746. https://doi.org/10.1021/ja400881n.

[6] P.M. Beaujuge, J.R. Reynolds, Color Control in π-Conjugated Organic Polymers for Use in Electrochromic Devices, Chem. Rev. 110 (2010) 268–320. https://doi.org/10.1021/cr900129a.

[7] D.T. McQuade, A.E. Pullen, T.M. Swager, Conjugated Polymer-Based Chemical Sensors, Chem. Rev. 100 (2000) 2537–2574. https://doi.org/10.1021/cr9801014.

[8] P. Lin, F. Yan, Organic Thin-Film Transistors for Chemical and Biological Sensing, Advanced Materials. 24 (2012) 34–51. https://doi.org/10.1002/adma.201103334.

[9] M.D. McGehee, A.J. Heeger, Semiconducting (Conjugated) Polymers as Materials for Solid-State Lasers, Advanced Materials. 12 (2000) 1655–1668. https://doi.org/10.1002/1521-4095(200011)12:22<1655::AID-ADMA1655>3.0.CO;2-2.

[10] B. Schmatz, R.M. Pankow, B.C. Thompson, J.R. Reynolds, Perspective on the advancements in conjugated polymer synthesis, design, and functionality over the past ten years., in: Conjugated Polym.: Perspect., Theory, New Mater., CRC Press, 2019: pp. 107–148.

[11] H. Sirringhaus, M. Bird, N. Zhao, Charge Transport Physics of Conjugated Polymer Field-Effect Transistors, Adv. Mater. 22 (2010) 3893–3898. https://doi.org/10.1002/adma.200902857.

[12] H. Li, G. Sini, J. Sit, A. Moule, J.-L. Bredas, Understanding Charge Transport in Donor/Acceptor Blends from Large-Scale Device Simulations Based on Experimental Film Morphologies, Energy Environ. Sci. (2020). https://doi.org/10.1039/C9EE03791H.
[13] J.-L. Bredas, D. Beljonne, V. Coropceanu, Jerome. Cornil, Charge-Transfer and Energy-Transfer Processes in π-Conjugated Oligomers and Polymers: A Molecular Picture., Chem. Rev. (Washington, DC, U. S.). 104 (2004) 4971–5003. https://doi.org/10.1021/cr040084k.
[14] V.D. Mihailetchi, L.J.A. Koster, J.C. Hummelen, P.W.M. Blom, Photocurrent Generation in Polymer-Fullerene Bulk Heterojunctions, Phys. Rev. Lett. 93 (2004) 216601. https://doi.org/10.1103/PhysRevLett.93.216601.
[15] H. Sirringhaus, Device Physics of Solution-Processed Organic Field-Effect Transistors, Advanced Materials. 17 (2005) 2411–2425. https://doi.org/10.1002/adma.200501152.
[16] S.C. Rasmussen, Electrically Conducting Plastics: Revising the History of Conjugated Organic Polymers, in: 100+ Years of Plastics. Leo Baekeland and Beyond, American Chemical Society, 2011: pp. 147–163. https://doi.org/10.1021/bk-2011-1080.ch010.
[17] A.J. Heeger, Semiconducting polymers: the Third Generation, Chem. Soc. Rev. 39 (2010) 2354–2371. https://doi.org/10.1039/B914956M.
[18] T.M. Swager, *50th Anniversary Perspective*: Conducting/Semiconducting Conjugated Polymers. A Personal Perspective on the Past and the Future, Macromolecules. (2017). https://doi.org/10.1021/acs.macromol.7b00582.
[19] S.C. Rasmussen, Early history of conjugated polymers: from their origins to the handbook of conducting polymers., in: Conjugated Polym.: Perspect., Theory, New Mater., CRC Press, 2019: pp. 1–35.
[20] S.C. Rasmussen, Conjugated and Conducting Organic Polymers: The First 150 Years, ChemPlusChem. 85 (2020) 1412–1429. https://doi.org/10.1002/cplu.202000325.
[21] C.K. Chiang, C.R. Fincher, Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, S.C. Gau, A.G. MacDiarmid, Electrical Conductivity in Doped Polyacetylene, Phys. Rev. Lett. 39 (1977) 1098–1101. https://doi.org/10.1103/PhysRevLett.39.1098.
[22] H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang, A.J. Heeger, Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH)x, J. Chem. Soc., Chem. Commun. (1977) 578–580. https://doi.org/10.1039/C39770000578.
[23] M.M. Labes, P. Love, L.F. Nichols, Polysulfur nitride - a metallic, superconducting polymer, Chem. Rev. 79 (1979) 1–15. https://doi.org/10.1021/cr60317a002.
[24] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J.R. Reynolds, Poly(3,4-ethylenedioxythiophene) and Its Derivatives: Past, Present, and Future, Advanced Materials. 12 (2000) 481–494. https://doi.org/10.1002/(SICI)1521-4095(200004)12:7<481::AID-ADMA481>3.0.CO;2-C.
[25] M. Bendikov, N. Martin, D.F. Perepichka, M. Prato, Fred Wudl. Discovering new science through making new molecules, J. Mater. Chem. 21 (2011) 1292–1294. https://doi.org/10.1039/C0JM90123G.
[26] Q. Zhang, D.F. Perepichka, Z. Bao, Fred Wudl's fifty-year contribution to organic semiconductors, J. Mater. Chem. C. 6 (2018) 3483–3484. https://doi.org/10.1039/C8TC90055H.
[27] S. Hotta, S.D.D.V. Rughooputh, A.J. Heeger, F. Wudl, Spectroscopic studies of soluble poly(3-alkylthienylenes), Macromolecules. 20 (1987) 212–215. https://doi.org/10.1021/ma00167a038.

[28] M. Kobayashi, J. Chen, T.-C. Chung, F. Moraes, A.J. Heeger, F. Wudl, Synthesis and properties of chemically coupled poly(thiophene), Synthetic Metals. 9 (1984) 77–86. https://doi.org/10.1016/0379-6779(84)90044-4.
[29] F. Wudl, M. Kobayashi, A.J. Heeger, Poly(isothianaphthene), J. Org. Chem. 49 (1984) 3382–3384. https://doi.org/10.1021/jo00192a027.
[30] A.O. Patil, Y. Ikenoue, F. Wudl, A.J. Heeger, Water soluble conducting polymers, J. Am. Chem. Soc. 109 (1987) 1858–1859. https://doi.org/10.1021/ja00240a044.
[31] F. Jonas, H. Gerard, W. Schmidtberg, Preparation of (alkylenedioxy)thiophene polymers for use as antistatic agents, DE 3813589, 1989.
[32] A. Elschner, S. Kirchmeyer, W. Lovenich, U. Merker, K. Reuter, PEDOT: Principles and Applications of an Intrinsically Conductive Polymer, 1st ed., CRC Press, Boca Raton, 2010.
[33] W.J. Feast, J. Tsibouklis, K.L. Pouwer, L. Groenendaal, E.W. Meijer, Synthesis, processing and material properties of conjugated polymers, Polymer. 37 (1996) 5017–5047. https://doi.org/10.1016/0032-3861(96)00439-9.
[34] J. Roncali, Conjugated poly(thiophenes): synthesis, functionalization, and applications, Chem. Rev. 92 (1992) 711–738. https://doi.org/10.1021/cr00012a009.
[35] R.N. McDonald, T.W. Campbell, The Wittig Reaction as a Polymerization Method1a, J. Am. Chem. Soc. 82 (1960) 4669–4671. https://doi.org/10.1021/ja01502a054.
[36] H.G. Gilch, Preparation of poly-p-xylylenes by electrolysis, Journal of Polymer Science Part A-1: Polymer Chemistry. 4 (1966) 1351–1357. https://doi.org/10.1002/pol.1966.150040603.
[37] M. Rehahn, A.-D. Schlüter, G. Wegner, W.J. Feast, Soluble poly(para-phenylene)s. 1. Extension of the Yamamoto synthesis to dibromobenzenes substituted with flexible side chains, Polymer. 30 (1989) 1054–1059. https://doi.org/10.1016/0032-3861(89)90078-5.
[38] T. Junkers, J. Vandenbergh, P. Adriaensens, L. Lutsen, D. Vanderzande, Synthesis of poly(p-phenylene vinylene) materials via the precursor routes, Polym. Chem. 3 (2012) 275–285. https://doi.org/10.1039/C1PY00345C.
[39] M. Rehahn, A.-D. Schlüter, Soluble poly(p-phenylenevinylene)s from 2,5-dihexylterephthalaldehyde using the improved McMurry reagent, Die Makromolekulare Chemie, Rapid Communications. 11 (1990) 375–379. https://doi.org/10.1002/marc.1990.030110806.
[40] A.M. Saxman, R. Liepins, M. Aldissi, Polyacetylene: Its synthesis, doping and structure, Progress in Polymer Science. 11 (1985) 57–89. https://doi.org/10.1016/0079-6700(85)90008-5.
[41] T. Yamamoto, A. Yamamoto, A NOVEL TYPE OF POLYCONDENSATION OF POLYHALOGENATED ORGANIC AROMATIC COMPOUNDS PRODUCING THERMOSTABLE POLYPHENYLENE TYPE POLYMERS PROMOTED BY NICKEL COMPLEXES, Chem. Lett. 6 (1977) 353–356. https://doi.org/10.1246/cl.1977.353.
[42] T. Yamamoto, Y. Hayashi, A. Yamamoto, A Novel Type of Polycondensation Utilizing Transition Metal-Catalyzed C–C Coupling. I. Preparation of Thermostable Polyphenylene Type Polymers, BCSJ. 51 (1978) 2091–2097. https://doi.org/10.1246/bcsj.51.2091.
[43] T. Yamamoto, Cross-coupling reactions for preparation of π-conjugated polymers, Journal of Organometallic Chemistry. 653 (2002) 195–199. https://doi.org/10.1016/S0022-328X(02)01261-5.
[44] B.C. Thompson, J.M.J. Frechet, Polymer-fullerene composite solar cells., Angew. Chem., Int. Ed. 47 (2008) 58–77. https://doi.org/10.1002/anie.200702506.

[45] C. Sekine, Y. Tsubata, T. Yamada, M. Kitano, S. Doi, Recent progress of high performance polymer OLED and OPV materials for organic printed electronics, Science and Technology of Advanced Materials. 15 (2014) 034203. https://doi.org/10.1088/1468-6996/15/3/034203.
[46] M.T. Bernius, M. Inbasekaran, J. O'Brien, W. Wu, Progress with Light-Emitting Polymers, Advanced Materials. 12 (2000) 1737–1750. https://doi.org/10.1002/1521-4095(200012)12:23<1737::AID-ADMA1737>3.0.CO;2-N.
[47] G. Yu, High performance photonic devices made with semiconducting polymers, Synthetic Metals. 80 (1996) 143–150. https://doi.org/10.1016/S0379-6779(96)03695-8.
[48] E.W.H. Jager, E. Smela, O. Inganäs, Microfabricating Conjugated Polymer Actuators, Science. 290 (2000) 1540. https://doi.org/10.1126/science.290.5496.1540.
[49] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns, A.B. Holmes, Light-emitting diodes based on conjugated polymers, Nature. 347 (1990) 539–541. https://doi.org/10.1038/347539a0.
[50] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A.D. Santos, J.L. Brédas, M. Lögdlund, W.R. Salaneck, Electroluminescence in conjugated polymers, Nature. 397 (1999) 121–128. https://doi.org/10.1038/16393.
[51] S.C. Moratti, R. Cervini, A.B. Holmes, D.R. Baigent, R.H. Friend, N.C. Greenham, J. Grüner, P.J. Hamer, High electron affinity polymers for LEDs, Synthetic Metals. 71 (1995) 2117–2120. https://doi.org/10.1016/0379-6779(94)03193-A.
[52] J.J.M. Halls, C.A. Walsh, N.C. Greenham, E.A. Marseglia, R.H. Friend, S.C. Moratti, A.B. Holmes, Efficient photodiodes from interpenetrating polymer networks, Nature. 376 (1995) 498–500. https://doi.org/10.1038/376498a0.
[53] M. Granström, K. Petritsch, A.C. Arias, A. Lux, M.R. Andersson, R.H. Friend, Laminated fabrication of polymeric photovoltaic diodes, Nature. 395 (1998) 257–260. https://doi.org/10.1038/26183.
[54] A. Kraft, A.C. Grimsdale, A.B. Holmes, Electroluminescent Conjugated Polymers—Seeing Polymers in a New Light, Angewandte Chemie International Edition. 37 (1998) 402–428. https://doi.org/10.1002/(SICI)1521-3773(19980302)37:4<402::AID-ANIE402>3.0.CO;2-9.
[55] X. Guo, M. Baumgarten, K. Müllen, Designing π-conjugated polymers for organic electronics, Progress in Polymer Science. 38 (2013) 1832–1908. https://doi.org/10.1016/j.progpolymsci.2013.09.005.
[56] A. Greiner, Design and synthesis of polymers for light-emitting diodes, Polymers for Advanced Technologies. 9 (1998) 371–389. https://doi.org/10.1002/(SICI)1099-1581(199807)9:7<371::AID-PAT817>3.0.CO;2-7.
[57] R. Jakubiak, C.J. Collison, W.C. Wan, L.J. Rothberg, B.R. Hsieh, Aggregation Quenching of Luminescence in Electroluminescent Conjugated Polymers, J. Phys. Chem. A. 103 (1999) 2394–2398. https://doi.org/10.1021/jp9839450.
[58] Y. Shi, J. Liu, Y. Yang, Device performance and polymer morphology in polymer light emitting diodes: The control of thin film morphology and device quantum efficiency, Journal of Applied Physics. 87 (2000) 4254–4263. https://doi.org/10.1063/1.373062.
[59] F. Motamedi, K.J. Ihn, Z. Ni, G. Srdanov, F. Wudl, P. Smith, Fibres of poly (methoxy-2-ethyl-hexyloxy) phenylenevinylene prepared from the soluble, fully conjugated polymer, Polymer. 33 (1992) 1102–1104. https://doi.org/10.1016/0032-3861(92)90030-Z.
[60] J. Mei, Z. Bao, Side Chain Engineering in Solution-Processable Conjugated Polymers, Chem. Mater. 26 (2014) 604–615. https://doi.org/10.1021/cm4020805.

[61] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions, Science. 270 (1995) 1789–1791. https://doi.org/10.1126/science.270.5243.1789.

[62] Paul C Dastoor, Warwick J Belcher, How the West was Won? A History of Organic Photovoltaics, Substantia. 3 (2019). https://doi.org/10.13128/Substantia-612.

[63] Q. Pei, Yang, Efficient Photoluminescence and Electroluminescence from a Soluble Polyfluorene, J. Am. Chem. Soc. 118 (1996) 7416–7417. https://doi.org/10.1021/ja9615233.

[64] M. Ranger, D. Rondeau, M. Leclerc, New Well-Defined Poly(2,7-fluorene) Derivatives: Photoluminescence and Base Doping, Macromolecules. 30 (1997) 7686–7691. https://doi.org/10.1021/ma970920a.

[65] H. Sirringhaus, R.J. Wilson, R.H. Friend, M. Inbasekaran, W. Wu, E.P. Woo, M. Grell, D.D.C. Bradley, Mobility enhancement in conjugated polymer field-effect transistors through chain alignment in a liquid-crystalline phase, Appl. Phys. Lett. 77 (2000) 406–408. https://doi.org/10.1063/1.126991.

[66] Z. Bao, J. Locklin, Organic Field-Effect Transistors, CRC Press, New York, 2007.

[67] H. Koezuka, A. Tsumura, T. Ando, Field-effect transistor with polythiophene thin film, Synthetic Metals. 18 (1987) 699–704. https://doi.org/10.1016/0379-6779(87)90964-7.

[68] E.E. Havinga, W. ten Hoeve, H. Wynberg, A new class of small band gap organic polymer conductors, Polymer Bulletin. 29 (1992) 119–126. https://doi.org/10.1007/BF00558045.

[69] E.E. Havinga, W. ten Hoeve, H. Wynberg, Alternate donor-acceptor small-band-gap semiconducting polymers; Polysquaraines and polycroconaines, Synthetic Metals. 55 (1993) 299–306. https://doi.org/10.1016/0379-6779(93)90949-W.

[70] Z.-H. Zhou, T. Maruyama, T. Kanbara, T. Ikeda, K. Ichimura, T. Yamamoto, K. Tokuda, Unique optical and electrochemical properties of π-conjugated electrically conducting copolymers consisting of electron-withdrawing pyridine units and electron-donating thiophene units, J. Chem. Soc., Chem. Commun. (1991) 1210–1212. https://doi.org/10.1039/C39910001210.

[71] Yasuhiko. Shirota, Organic materials for electronic and optoelectronic devices., J. Mater. Chem. 10 (2000) 1–25. https://doi.org/10.1039/a908130e.

[72] A. Kumar, D.M. Welsh, M.C. Morvant, F. Piroux, K.A. Abboud, J.R. Reynolds, Conducting Poly(3,4-alkylenedioxythiophene) Derivatives as Fast Electrochromics with High-Contrast Ratios, Chem. Mater. 10 (1998) 896–902. https://doi.org/10.1021/cm9706614.

[73] D.M. Welsh, A. Kumar, E.W. Meijer, J.R. Reynolds, Enhanced Contrast Ratios and Rapid Switching in Electrochromics Based on Poly(3,4-propylenedioxythiophene) Derivatives, Advanced Materials. 11 (1999) 1379–1382. https://doi.org/10.1002/(SICI)1521-4095(199911)11:16<1379::AID-ADMA1379>3.0.CO;2-Q.

[74] B. Sankaran, J.R. Reynolds, High-Contrast Electrochromic Polymers from Alkyl-Derivatized Poly(3,4-ethylenedioxythiophenes), Macromolecules. 30 (1997) 2582–2588. https://doi.org/10.1021/ma961607w.

[75] G.A. Sotzing, J.R. Reynolds, P.J. Steel, Electrochromic Conducting Polymers via Electrochemical Polymerization of Bis(2-(3,4-ethylenedioxy)thienyl) Monomers, Chem. Mater. 8 (1996) 882–889. https://doi.org/10.1021/cm9504798.

[76] M. Dietrich, J. Heinze, G. Heywang, F. Jonas, Electrochemical and spectroscopic characterization of polyalkylenedioxythiophenes, Journal of Electroanalytical Chemistry. 369 (1994) 87–92. https://doi.org/10.1016/0022-0728(94)87085-3.

[77] S. Akoudad, J. Roncali, Electrochemical synthesis of poly(3,4-ethylenedioxythiophene) from a dimer precursor, Synthetic Metals. 93 (1998) 111–114. https://doi.org/10.1016/S0379-6779(97)04100-3.
[78] Z. Bao, W. Chan, L. Yu, Synthesis of conjugated polymer by the Stille Coupling Reaction, Chem. Mater. 5 (1993) 2–3. https://doi.org/10.1021/cm00025a001.
[79] Z. Bao, W.K. Chan, L. Yu, Exploration of the Stille Coupling Reaction for the Synthesis of Functional Polymers, J. Am. Chem. Soc. 117 (1995) 12426–12435. https://doi.org/10.1021/ja00155a007.
[80] J. Sakamoto, M. Rehahn, G. Wegner, A.D. Schlüter, Suzuki Polycondensation: Polyarylenes à la Carte, Macromol. Rapid. Commun. 30 (2009) 653–687. https://doi.org/10.1002/marc.200900063.
[81] Z. Bao, Y. Chen, R. Cai, L. Yu, Conjugated liquid-crystalline polymers - soluble and fusible poly(phenylenevinylene) by the Heck coupling reaction, Macromolecules. 26 (1993) 5281–5286. https://doi.org/10.1021/ma00072a002.
[82] C. Cordovilla, C. Bartolomé, J.M. Martínez-Ilarduya, P. Espinet, The Stille Reaction, 38 Years Later, ACS Catal. 5 (2015) 3040–3053. https://doi.org/10.1021/acscatal.5b00448.
[83] Norio. Miyaura, Akira. Suzuki, Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds, Chem. Rev. 95 (1995) 2457–2483. https://doi.org/10.1021/cr00039a007.
[84] V. Farina, V. Krishnamurthy, W.J. Scott, The Stille Reaction, in: Organic Reactions, American Cancer Society, 2004: pp. 1–652. https://doi.org/10.1002/0471264180.or050.01.
[85] A.B. Dounay, L.E. Overman, The Asymmetric Intramolecular Heck Reaction in Natural Product Total Synthesis, Chem. Rev. 103 (2003) 2945–2964. https://doi.org/10.1021/cr020039h.
[86] M. Karikomi, C. Kitamura, S. Tanaka, Y. Yamashita, New Narrow-Bandgap Polymer Composed of Benzobis(1,2,5-thiadiazole) and Thiophenes, J. Am. Chem. Soc. 117 (1995) 6791–6792. https://doi.org/10.1021/ja00130a024.
[87] S. Tanaka, Y. Yamashita, Syntheses of narrow band gap heterocyclic copolymers of aromatic-donor and quinonoid-acceptor units, Synthetic Metals. 69 (1995) 599–600. https://doi.org/10.1016/0379-6779(94)02587-O.
[88] T. Yamamoto, Z. Zhou, T. Kanbara, M. Shimura, K. Kizu, T. Maruyama, Y. Nakamura, T. Fukuda, B.-L. Lee, N. Ooba, S. Tomaru, T. Kurihara, T. Kaino, K. Kubota, S. Sasaki, π-Conjugated Donor−Acceptor Copolymers Constituted of π-Excessive and π-Deficient Arylene Units. Optical and Electrochemical Properties in Relation to CT Structure of the Polymer, J. Am. Chem. Soc. 118 (1996) 10389–10399. https://doi.org/10.1021/ja961550t.
[89] M. Rehahn, A.-D. Schlüter, G. Wegner, W.J. Feast, Soluble poly(para-phenylene)s. 2. Improved synthesis of poly(para-2,5-di-n-hexylphenylene) via Pd-catalysed coupling of 4-bromo-2,5-di-n-hexylbenzeneboronic acid, Polymer. 30 (1989) 1060–1062. https://doi.org/10.1016/0032-3861(89)90079-7.
[90] A.J. J. Lennox, G. C. Lloyd-Jones, Selection of boron reagents for Suzuki–Miyaura coupling, Chemical Society Reviews. 43 (2014) 412–443. https://doi.org/10.1039/C3CS60197H.
[91] T. Yamamoto, T. Maruyama, Z.-H. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, .pi.-Conjugated Poly(pyridine-2,5-diyl), Poly(2,2'-bipyridine-5,5'-diyl), and Their Alkyl Derivatives. Preparation, Linear Structure, Function as a Ligand to Form Their Transition Metal Complexes, Catalytic Reactions, n-Type Electrically Conducting

Properties, Optical Properties, and Alignment on Substrates, J. Am. Chem. Soc. 116 (1994) 4832–4845. https://doi.org/10.1021/ja00090a031.
[92] T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z.H. Zhou, Y. Nakamura, T. Kanbara, S. Sasaki, K. Kubota, Preparation of π-conjugated poly(thiophene-2,5-diyl), poly(p-phenylene), and related polymers using zerovalent nickel complexes. Linear structure and properties of the π-conjugated polymers, Macromolecules. 25 (1992) 1214–1223. https://doi.org/10.1021/ma00030a003.
[93] R.D. McCullough, R.D. Lowe, Enhanced electrical conductivity in regioselectively synthesized poly(3-alkylthiophenes), J. Chem. Soc., Chem. Commun. (1992) 70–72. https://doi.org/10.1039/C39920000070.
[94] T.A. Chen, R.D. Rieke, The first regioregular head-to-tail poly(3-hexylthiophene-2,5-diyl) and a regiorandom isopolymer: nickel versus palladium catalysis of 2(5)-bromo-5(2)-(bromozincio)-3-hexylthiophene polymerization, J. Am. Chem. Soc. 114 (1992) 10087–10088. https://doi.org/10.1021/ja00051a066.
[95] T.-A. Chen, X. Wu, R.D. Rieke, Regiocontrolled Synthesis of Poly(3-alkylthiophenes) Mediated by Rieke Zinc: Their Characterization and Solid-State Properties, J. Am. Chem. Soc. 117 (1995) 233–244. https://doi.org/10.1021/ja00106a027.
[96] R.D. McCullough, The Chemistry of Conducting Polythiophenes, Adv. Mater. 10 (1998) 93–116. https://doi.org/10.1002/(SICI)1521-4095(199801)10:2<93::AID-ADMA93>3.0.CO;2-F.
[97] R.S. Loewe, S.M. Khersonsky, R.D. McCullough, A Simple Method to Prepare Head-to-Tail Coupled, Regioregular Poly(3-alkylthiophenes) Using Grignard Metathesis, Advanced Materials. 11 (1999) 250–253. https://doi.org/10.1002/(SICI)1521-4095(199903)11:3<250::AID-ADMA250>3.0.CO;2-J.
[98] M. Se´vignon, J. Papillon, E. Schulz, M. Lemaire, New synthetic method for the polymerization of alkylthiophenes, Tetrahedron Letters. 40 (1999) 5873–5876. https://doi.org/10.1016/S0040-4039(99)01164-8.
[99] A. Facchetti, π-Conjugated Polymers for Organic Electronics and Photovoltaic Cell Applications†, Chem. Mater. 23 (2010) 733–758. https://doi.org/10.1021/cm102419z.
[100] N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletête, G. Durocher, Y. Tao, M. Leclerc, Toward a Rational Design of Poly(2,7-Carbazole) Derivatives for Solar Cells, J. Am. Chem. Soc. 130 (2008) 732–742. https://doi.org/10.1021/ja0771989.
[101] M.J. Robb, S.-Y. Ku, F.G. Brunetti, C.J. Hawker, A renaissance of color: New structures and building blocks for organic electronics, J. Polym. Sci. A Polym. Chem. 51 (2013) 1263–1271. https://doi.org/10.1002/pola.26531.
[102] Y.-J. Cheng, S.-H. Yang, C.-S. Hsu, Synthesis of Conjugated Polymers for Organic Solar Cell Applications, Chem. Rev. 109 (2009) 5868–5923. https://doi.org/10.1021/cr900182s.
[103] D. Gedefaw, M.R. Andersson, Donor-acceptor polymers for organic photovoltaics., in: Conjugated Polym.: Perspect., Theory, New Mater., CRC Press, 2019: pp. 283–323.
[104] H. Sirringhaus, 25th Anniversary Article: Organic Field-Effect Transistors: The Path Beyond Amorphous Silicon, Adv. Mater. 26 (2014) 1319–1335. https://doi.org/10.1002/adma.201304346.
[105] X. Guo, A. Facchetti, T.J. Marks, Imide- and Amide-Functionalized Polymer Semiconductors., Chem. Rev. 114 (2014) 8943–9021. https://doi.org/10.1021/cr500225d.

[106] F. Huang, H. Wu, D. Wang, W. Yang, Y. Cao, Novel Electroluminescent Conjugated Polyelectrolytes Based on Polyfluorene, Chem. Mater. 16 (2004) 708–716. https://doi.org/10.1021/cm034650o.

[107] F. Huang, H. Wu, Y. Cao, Water/alcohol soluble conjugated polymers as highly efficient electron transporting/injection layer in optoelectronic devices, Chem. Soc. Rev. 39 (2010) 2500–2521. https://doi.org/10.1039/B907991M.

[108] X. Zhao, M.R. Pinto, L.M. Hardison, J. Mwaura, J. Müller, H. Jiang, D. Witker, V.D. Kleiman, J.R. Reynolds, K.S. Schanze, Variable Band Gap Poly(arylene ethynylene) Conjugated Polyelectrolytes, Macromolecules. 39 (2006) 6355–6366. https://doi.org/10.1021/ma0611523.

[109] I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M.L. Chabinyc, R.J. Kline, M.D. McGehee, M.F. Toney, Liquid-crystalline semiconducting polymers with high charge-carrier mobility, Nature Materials. 5 (2006) 328–333. https://doi.org/10.1038/nmat1612.

[110] H. Sirringhaus, P.J. Brown, R.H. Friend, M.M. Nielsen, K. Bechgaard, B.M.W. Langeveld-Voss, A.J.H. Spiering, R. a. J. Janssen, E.W. Meijer, P. Herwig, D.M. de Leeuw, Two-dimensional charge transport in self-organized, high-mobility conjugated polymers, Nature. 401 (1999) 685–688. https://doi.org/10.1038/44359.

[111] B.H. Hamadani, D.J. Gundlach, I. McCulloch, M. Heeney, Undoped polythiophene field-effect transistors with mobility of 1cm2V−1s−1, Appl. Phys. Lett. 91 (2007) 243512. https://doi.org/10.1063/1.2824845.

[112] I. McCulloch, M. Heeney, M.L. Chabinyc, D. DeLongchamp, R.J. Kline, M. Cölle, W. Duffy, D. Fischer, D. Gundlach, B. Hamadani, R. Hamilton, L. Richter, A. Salleo, M. Shkunov, D. Sparrowe, S. Tierney, W. Zhang, Semiconducting Thienothiophene Copolymers: Design, Synthesis, Morphology, and Performance in Thin-Film Organic Transistors, Advanced Materials. 21 (2009) 1091–1109. https://doi.org/10.1002/adma.200801650.

[113] Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray, L. Yu, Highly Efficient Solar Cell Polymers Developed via Fine-Tuning of Structural and Electronic Properties, J. Am. Chem. Soc. 131 (2009) 7792–7799. https://doi.org/10.1021/ja901545q.

[114] Y. Liang, Y. Wu, D. Feng, S.-T. Tsai, H.-J. Son, G. Li, L. Yu, Development of New Semiconducting Polymers for High Performance Solar Cells, J. Am. Chem. Soc. 131 (2009) 56–57. https://doi.org/10.1021/ja808373p.

[115] M. Pomerantz, X. Gu, S.X. Zhang, Poly(2-decylthieno[3,4-b]thiophene-4,6-diyl). A New Low Band Gap Conducting Polymer, Macromolecules. 34 (2001) 1817–1822. https://doi.org/10.1021/ma001696j.

[116] Y. Liang, L. Yu, A New Class of Semiconducting Polymers for Bulk Heterojunction Solar Cells with Exceptionally High Performance, Acc. Chem. Res. 43 (2010) 1227–1236. https://doi.org/10.1021/ar1000296.

[117] H. Pan, Y. Li, Y. Wu, P. Liu, B.S. Ong, S. Zhu, G. Xu, Synthesis and Thin-Film Transistor Performance of Poly(4,8-didodecylbenzo[1,2-b:4,5-b‘]dithiophene), Chem. Mater. 18 (2006) 3237–3241. https://doi.org/10.1021/cm0602592.

[118] K. Shiraishi, T. Yamamoto, New π-conjugated polymers constituted of dialkoxybenzodithiophene units: synthesis and electronic properties, Synthetic Metals. 130 (2002) 139–147. https://doi.org/10.1016/S0379-6779(02)00078-4.

[119] G. Koßmehl, P. Beimling, G. Manecke, Über polyarylenalkenylene und polyheteroarylenalkenylene, 14. Synthesen und charakterisierung von poly(thieno[2′,3′:1,2]benzo[4,5-b]thiophen-2,6-diylvinylenarylenvinylen)en, poly(4,8-dimethoxythieno[2′,3′:1,2]benzo[4,5-b]thiophen-2,6-diylvinylenarylenvinylen)en und einigen modellverbindungen, Makromol. Chem. 184 (1983) 627–650. https://doi.org/10.1002/macp.1983.021840317.
[120] J. Hou, M.-H. Park, S. Zhang, Y. Yao, L.-M. Chen, J.-H. Li, Y. Yang, Bandgap and Molecular Energy Level Control of Conjugated Polymer Photovoltaic Materials Based on Benzo[1,2-b:4,5-b′]dithiophene, Macromolecules. 41 (2008) 6012–6018. https://doi.org/10.1021/ma800820r.
[121] J. Hou, H.-Y. Chen, S. Zhang, G. Li, Yang. Yang, Synthesis, Characterization, and Photovoltaic Properties of a Low Band Gap Polymer Based on Silole-Containing Polythiophenes and 2,1,3-Benzothiadiazole., J. Am. Chem. Soc. 130 (2008) 16144–16145. https://doi.org/10.1021/ja806687u.
[122] E. Wang, L. Wang, L. Lan, C. Luo, W. Zhuang, J. Peng, Y. Cao, High-performance polymer heterojunction solar cells of a polysilafluorene derivative, Appl. Phys. Lett. 92 (2008) 033307. https://doi.org/10.1063/1.2836266.
[123] T. Baumgartner, R. Réau, Organophosphorus π-Conjugated Materials, Chem. Rev. 106 (2006) 4681–4727. https://doi.org/10.1021/cr040179m.
[124] J. Chen, Y. Cao, Silole-Containing Polymers: Chemistry and Optoelectronic Properties, Macromol. Rapid Commun. 28 (2007) 1714–1742. https://doi.org/10.1002/marc.200700326.
[125] A.M. Priegert, B.W. Rawe, S.C. Serin, D.P. Gates, Polymers and the p-block elements, Chem. Soc. Rev. 45 (2016) 922–953. https://doi.org/10.1039/C5CS00725A.
[126] S.M. Parke, M.P. Boone, E. Rivard, Marriage of heavy main group elements with [small pi]-conjugated materials for optoelectronic applications, Chem. Commun. 52 (2016) 9485–9505. https://doi.org/10.1039/C6CC04023C.
[127] N. Matsumi, Yoshiki. Chujo, π-Conjugated organoboron polymers via the vacant p-orbital of the boron atom., Polym. J. (Tokyo, Jpn.). 40 (2008) 77–89. https://doi.org/10.1295/polymj.PJ2007170.
[128] G.L. Gibson, T.M. McCormick, D.S. Seferos, Effect of Group-14 and Group-16 Substitution on the Photophysics of Structurally Related Donor-Acceptor Polymers., J. Phys. Chem. C. 117 (2013) 16606–16615. https://doi.org/10.1021/jp405257r.
[129] R. Stalder, J. Mei, K.R. Graham, L.A. Estrada, J.R. Reynolds, Isoindigo, a Versatile Electron-Deficient Unit For High-Performance Organic Electronics, Chem. Mater. 26 (2014) 664–678. https://doi.org/10.1021/cm402219v.
[130] C.B. Nielsen, M. Turbiez, I. McCulloch, Recent Advances in the Development of Semiconducting DPP-Containing Polymers for Transistor Applications, Adv. Mater. 25 (2013) 1859–1880. https://doi.org/10.1002/adma.201201795.
[131] M.M. Wienk, M. Turbiez, J. Gilot, R.A.J. Janssen, Narrow-Bandgap Diketo-Pyrrolo-Pyrrole Polymer Solar Cells: The Effect of Processing on the Performance, Advanced Materials. 20 (2008) 2556–2560. https://doi.org/10.1002/adma.200800456.
[132] C. Lee, S. Lee, G.-U. Kim, W. Lee, B.J. Kim, Recent Advances, Design Guidelines, and Prospects of All-Polymer Solar Cells, Chem. Rev. 119 (2019) 8028–8086. https://doi.org/10.1021/acs.chemrev.9b00044.
[133] Z. Chen, Y. Zheng, H. Yan, A. Facchetti, Naphthalenedicarboximide- vs Perylenedicarboximide-Based Copolymers. Synthesis and Semiconducting Properties in

Bottom-Gate N-Channel Organic Transistors, J. Am. Chem. Soc. 131 (2009) 8–9. https://doi.org/10.1021/ja805407g.

[134] H. Yan, Z. Chen, Y. Zheng, C. Newman, J.R. Quinn, F. Dötz, M. Kastler, A. Facchetti, A high-mobility electron-transporting polymer for printed transistors, Nature. 457 (2009) 679–686. https://doi.org/10.1038/nature07727.

[135] Y. Zou, A. Najari, P. Berrouard, S. Beaupré, B. Réda Aïch, Y. Tao, M. Leclerc, A Thieno[3,4-c]pyrrole-4,6-dione-Based Copolymer for Efficient Solar Cells, J. Am. Chem. Soc. 132 (2010) 5330–5331. https://doi.org/10.1021/ja101888b.

[136] N. Blouin, A. Michaud, M. Leclerc, A Low-Bandgap Poly(2,7-Carbazole) Derivative for Use in High-Performance Solar Cells, Advanced Materials. 19 (2007) 2295–2300. https://doi.org/10.1002/adma.200602496.

[137] S.H. Park, A. Roy, S. Beaupré, S. Cho, N. Coates, J.S. Moon, D. Moses, M. Leclerc, K. Lee, A.J. Heeger, Bulk heterojunction solar cells with internal quantum efficiency approaching 100%, Nat Photon. 3 (2009) 297–302. https://doi.org/10.1038/nphoton.2009.69.

[138] E. Wang, L. Hou, Z. Wang, S. Hellström, F. Zhang, O. Inganäs, M.R. Andersson, An Easily Synthesized Blue Polymer for High-Performance Polymer Solar Cells, Advanced Materials. 22 (2010) 5240–5244. https://doi.org/10.1002/adma.201002225.

[139] A. Tanimoto, T. Yamamoto, Nickel-2,2′-Bipyridyl and Palladium-Triphenylphosphine Complex Promoted Synthesis of New π-Conjugated Poly(2-hexylbenzotriazole)s and Characterization of the Polymers, Advanced Synthesis & Catalysis. 346 (2004) 1818–1823. https://doi.org/10.1002/adsc.200404227.

[140] Q. Wang, R. Takita, Y. Kikuzaki, F. Ozawa, Palladium-Catalyzed Dehydrohalogenative Polycondensation of 2-Bromo-3-hexylthiophene: An Efficient Approach to Head-to-Tail Poly(3-hexylthiophene), J. Am. Chem. Soc. 132 (2010) 11420–11421. https://doi.org/10.1021/ja105767z.

[141] M. Nikolka, Henning. Sirringhaus, Conjugated polymer-based OFET devices., in: Conjugated Polym.: Prop., Process., Appl., CRC Press, 2019: pp. 1–19. https://www.crcpress.com/Conjugated-Polymers-Properties-Processing-and-Applications/Reynolds-Thompson-Skotheim/p/book/9781138065703.

[142] C. Wang, H. Dong, W. Hu, Y. Liu, Daoben. Zhu, Semiconducting π-Conjugated Systems in Field-Effect Transistors: A Material Odyssey of Organic Electronics., Chem. Rev. (Washington, DC, U. S.). 112 (2012) 2208–2267. https://doi.org/10.1021/cr100380z.

[143] T. Yokozawa, Y. Ohta, Chapter 1 Controlled Synthesis of Conjugated Polymers in Catalyst-transfer Condensation Polymerization: Monomers and Catalysts, in: Semiconducting Polymers: Controlled Synthesis and Microstructure, The Royal Society of Chemistry, 2017: pp. 1–37. https://doi.org/10.1039/9781782624004-00001.

[144] M.P. Aplan, E.D. Gomez, Recent Developments in Chain-Growth Polymerizations of Conjugated Polymers., Ind. Eng. Chem. Res. 56 (2017) 7888–7901. https://doi.org/10.1021/acs.iecr.7b01030.

[145] Z. Bao, A. Dodabalapur, A.J. Lovinger, Soluble and processable regioregular poly(3-hexylthiophene) for thin film field-effect transistor applications with high mobility, Appl. Phys. Lett. 69 (1996) 4108–4110. https://doi.org/10.1063/1.117834.

[146] M. Raja, G.C.R. Lloyd, N. Sedghi, W. Eccleston, R. Di Lucrezia, S.J. Higgins, Conduction processes in conjugated, highly regio-regular, high molecular mass, poly(3-hexylthiophene) thin-film transistors, Journal of Applied Physics. 92 (2002) 1441–1445. https://doi.org/10.1063/1.1490622.

[147] H.A. Bronstein, C.K. Luscombe, Externally Initiated Regioregular P3HT with Controlled Molecular Weight and Narrow Polydispersity, J. Am. Chem. Soc. 131 (2009) 12894–12895. https://doi.org/10.1021/ja9054977.
[148] K. Okamoto, C.K. Luscombe, Controlled polymerizations for the synthesis of semiconducting conjugated polymers, Polym. Chem. 2 (2011) 2424–2434. https://doi.org/10.1039/C1PY00171J.
[149] V. Senkovskyy, N. Khanduyeva, H. Komber, U. Oertel, M. Stamm, D. Kuckling, A. Kiriy, Conductive Polymer Brushes of Regioregular Head-to-Tail Poly(3-alkylthiophenes) via Catalyst-Transfer Surface-Initiated Polycondensation, J. Am. Chem. Soc. 129 (2007) 6626–6632. https://doi.org/10.1021/ja0710306.
[150] N. Khanduyeva, V. Senkovskyy, T. Beryozkina, V. Bocharova, F. Simon, M. Nitschke, M. Stamm, R. Grötzschel, A. Kiriy, Grafting of Poly(3-hexylthiophene) from Poly(4-bromostyrene) Films by Kumada Catalyst-Transfer Polycondensation: Revealing of the Composite Films Structure, Macromolecules. 41 (2008) 7383–7389. https://doi.org/10.1021/ma800889c.
[151] T. Yokozawa, Y. Nanashima, Y. Ohta, Precision Synthesis of n-Type π-Conjugated Polymers in Catalyst-Transfer Condensation Polymerization, ACS Macro Lett. 1 (2012) 862–866. https://doi.org/10.1021/mz300277s.
[152] R.S. Loewe, S.M. Khersonsky, R.D. McCullough, A Simple Method to Prepare Head-to-Tail Coupled, Regioregular Poly(3-alkylthiophenes) Using Grignard Metathesis, Adv. Mater. 11 (1999) 250–253. https://doi.org/10.1002/(SICI)1521-4095(199903)11:3<250::AID-ADMA250>3.0.CO;2-J.
[153] E.E. Sheina, J. Liu, M.C. Iovu, D.W. Laird, R.D. McCullough, Chain Growth Mechanism for Regioregular Nickel-Initiated Cross-Coupling Polymerizations, Macromolecules. 37 (2004) 3526–3528. https://doi.org/10.1021/ma0357063.
[154] M.C. Iovu, E.E. Sheina, R.R. Gil, R.D. McCullough, Experimental Evidence for the Quasi-"Living" Nature of the Grignard Metathesis Method for the Synthesis of Regioregular Poly(3-alkylthiophenes), Macromolecules. 38 (2005) 8649–8656. https://doi.org/10.1021/ma051122k.
[155] A. Kiriy, V. Senkovskyy, M. Sommer, Kumada Catalyst-Transfer Polycondensation: Mechanism, Opportunities, and Challenges, Macromol. Rapid Commun. 32 (2011) 1503–1517. https://doi.org/10.1002/marc.201100316.
[156] R. Miyakoshi, K. Shimono, A. Yokoyama, T. Yokozawa, Catalyst-Transfer Polycondensation for the Synthesis of Poly(p-phenylene) with Controlled Molecular Weight and Low Polydispersity, J. Am. Chem. Soc. 128 (2006) 16012–16013. https://doi.org/10.1021/ja067107s.
[157] A. Yokoyama, H. Suzuki, Y. Kubota, K. Ohuchi, H. Higashimura, T. Yokozawa, Chain-Growth Polymerization for the Synthesis of Polyfluorene via Suzuki–Miyaura Coupling Reaction from an Externally Added Initiator Unit, J. Am. Chem. Soc. 129 (2007) 7236–7237. https://doi.org/10.1021/ja070313v.
[158] Y. Sun, H. Fu, Z. Wang, Polymer Donors for High-performance Non-fullerene Organic Solar Cells, Angewandte Chemie International Edition. 0 (2018). https://doi.org/10.1002/anie.201806291.
[159] Y. Cai, L. Huo, Y. Sun, Recent Advances in Wide-Bandgap Photovoltaic Polymers, Advanced Materials. (2017) 1605437. https://doi.org/10.1002/adma.201605437.

[160] Z. Li, C.-C. Chueh, A.K.-Y. Jen, Recent advances in molecular design of functional conjugated polymers for high-performance polymer solar cells, Progress in Polymer Science. 99 (2019) 101175. https://doi.org/10.1016/j.progpolymsci.2019.101175.
[161] C. An, Z. Zheng, J. Hou, Recent progress in wide bandgap conjugated polymer donors for high-performance nonfullerene organic photovoltaics, Chem. Commun. (2020). https://doi.org/10.1039/D0CC01038C.
[162] H. Yao, L. Ye, H. Zhang, S. Li, S. Zhang, J. Hou, Molecular Design of Benzodithiophene-Based Organic Photovoltaic Materials, Chem. Rev. 116 (2016) 7397–7457. https://doi.org/10.1021/acs.chemrev.6b00176.
[163] T. Ameri, P. Khoram, J. Min, C.J. Brabec, Organic Ternary Solar Cells: A Review, Adv. Mater. 25 (2013) 4245–4266. https://doi.org/10.1002/adma.201300623.
[164] Q. An, F. Zhang, J. Zhang, W. Tang, Z. Deng, B. Hu, Versatile ternary organic solar cells: a critical review, Energy Environ. Sci. 9 (2016) 281–322. https://doi.org/10.1039/C5EE02641E.
[165] N. Gasparini, A. Salleo, I. McCulloch, D. Baran, The role of the third component in ternary organic solar cells, Nature Reviews Materials. (2019). https://doi.org/10.1038/s41578-019-0093-4.
[166] B. Sun, W. Hong, Z. Yan, H. Aziz, Y. Li, Record High Electron Mobility of 6.3 cm2V−1s−1 Achieved for Polymer Semiconductors Using a New Building Block, Adv. Mater. 26 (2014) 2636–2642. https://doi.org/10.1002/adma.201305981.
[167] W. Li, K.H. Hendriks, A. Furlan, M.M. Wienk, R.A.J. Janssen, High Quantum Efficiencies in Polymer Solar Cells at Energy Losses below 0.6 eV, J. Am. Chem. Soc. 137 (2015) 2231–2234. https://doi.org/10.1021/ja5131897.
[168] Y. Li, H. Meng, T. Liu, Y. Xiao, Z. Tang, B. Pang, Y. Li, Y. Xiang, G. Zhang, X. Lu, G. Yu, H. Yan, C. Zhan, J. Huang, J. Yao, 8.78% Efficient All-Polymer Solar Cells Enabled by Polymer Acceptors Based on a B←N Embedded Electron-Deficient Unit, Advanced Materials. 31 (2019) 1904585. https://doi.org/10.1002/adma.201904585.
[169] H. Sun, F. Chen, Z.-K. Chen, Recent progress on non-fullerene acceptors for organic photovoltaics, Materials Today. 24 (2019) 94–118. https://doi.org/10.1016/j.mattod.2018.09.004.
[170] S. Zhang, L. Ye, J. Hou, Breaking the 10% Efficiency Barrier in Organic Photovoltaics: Morphology and Device Optimization of Well-Known PBDTTT Polymers, Adv. Energy Mater. 6 (2016) 201502529. https://doi.org/10.1002/aenm.201502529.
[171] H. Zhang, H. Yao, J. Hou, J. Zhu, J. Zhang, W. Li, R. Yu, B. Gao, S. Zhang, J. Hou, Over 14% Efficiency in Organic Solar Cells Enabled by Chlorinated Nonfullerene Small-Molecule Acceptors, Advanced Materials. 30 (2018) 1800613. https://doi.org/10.1002/adma.201800613.
[172] D. Qian, W. Ma, Z. Li, X. Guo, S. Zhang, L. Ye, H. Ade, Z. Tan, J. Hou, Molecular Design toward Efficient Polymer Solar Cells with High Polymer Content, J. Am. Chem. Soc. 135 (2013) 8464–8467. https://doi.org/10.1021/ja402971d.
[173] Y. Ie, J. Huang, Y. Uetani, M. Karakawa, Y. Aso, Synthesis, Properties, and Photovoltaic Performances of Donor–Acceptor Copolymers Having Dioxocycloalkene-Annelated Thiophenes As Acceptor Monomer Units, Macromolecules. 45 (2012) 4564–4571. https://doi.org/10.1021/ma300742r.
[174] Q. Wan, X. Guo, Z. Wang, W. Li, B. Guo, W. Ma, M. Zhang, Y. Li, 10.8% Efficiency Polymer Solar Cells Based on PTB7-Th and PC71BM via Binary Solvent Additives

Treatment, Adv. Funct. Mater. 26 (2016) 6635–6640. https://doi.org/10.1002/adfm.201602181.
[175] Y. Li, L. Zhong, B. Gautam, H.-J. Bin, J.-D. Lin, F.-P. Wu, Z. Zhang, Z.-Q. Jiang, Z.-G. Zhang, K. Gundogdu, Y. Li, L.-S. Liao, A near-infrared non-fullerene electron acceptor for high performance polymer solar cells, Energy Environ. Sci. 10 (2017) 1610–1620. https://doi.org/10.1039/C7EE00844A.
[176] L. Ye, S. Zhang, L. Huo, M. Zhang, J. Hou, Molecular Design toward Highly Efficient Photovoltaic Polymers Based on Two-Dimensional Conjugated Benzodithiophene, Acc. Chem. Res. 47 (2014) 1595–1603. https://doi.org/10.1021/ar5000743.
[177] R. Duan, L. Ye, X. Guo, Y. Huang, P. Wang, S. Zhang, J. Zhang, L. Huo, J. Hou, Application of Two-Dimensional Conjugated Benzo[1,2-b:4,5-b′]dithiophene in Quinoxaline-Based Photovoltaic Polymers, Macromolecules. 45 (2012) 3032–3038. https://doi.org/10.1021/ma300060z.
[178] Q. Wang, M. Li, X. Zhang, Y. Qin, J. Wang, J. Zhang, J. Hou, R.A.J. Janssen, Y. Geng, Carboxylate-Substituted Polythiophenes for Efficient Fullerene-Free Polymer Solar Cells: The Effect of Chlorination on Their Properties, Macromolecules. 52 (2019) 4464–4474. https://doi.org/10.1021/acs.macromol.9b00793.
[179] A. Zhang, C. Xiao, Y. Wu, C. Li, Y. Ji, L. Li, W. Hu, Z. Wang, W. Ma, W. Li, Effect of Fluorination on Molecular Orientation of Conjugated Polymers in High Performance Field-Effect Transistors, Macromolecules. 49 (2016) 6431–6438. https://doi.org/10.1021/acs.macromol.6b01446.
[180] Y. Zhang, H. Yao, S. Zhang, Y. Qin, J. Zhang, L. Yang, W. Li, Z. Wei, F. Gao, J. Hou, Fluorination vs. chlorination: a case study on high performance organic photovoltaic materials, Science China Chemistry. 61 (2018) 1328–1337. https://doi.org/10.1007/s11426-018-9260-2.
[181] X. Xu, K. Feng, Z. Bi, W. Ma, G. Zhang, Q. Peng, Single-Junction Polymer Solar Cells with 16.35% Efficiency Enabled by a Platinum(II) Complexation Strategy, Advanced Materials. 31 (2019) 1901872. https://doi.org/10.1002/adma.201901872.
[182] R. Po, G. Bianchi, C. Carbonera, A. Pellegrino, "All That Glisters Is Not Gold": An Analysis of the Synthetic Complexity of Efficient Polymer Donors for Polymer Solar Cells, Macromolecules. 48 (2015) 453–461. https://doi.org/10.1021/ma501894w.
[183] M. Zhang, X. Guo, W. Ma, H. Ade, J. Hou, A Polythiophene Derivative with Superior Properties for Practical Application in Polymer Solar Cells, Adv. Mater. 26 (2014) 5880–5885. https://doi.org/10.1002/adma.201401494.
[184] Y. Qin, M.A. Uddin, Y. Chen, B. Jang, K. Zhao, Z. Zheng, R. Yu, T.J. Shin, H.Y. Woo, J. Hou, Highly Efficient Fullerene-Free Polymer Solar Cells Fabricated with Polythiophene Derivative, Advanced Materials. 28 (2016) 9416–9422. https://doi.org/10.1002/adma.201601803.
[185] S.-J. Ko, Q.V. Hoang, C.E. Song, M.A. Uddin, E. Lim, S.Y. Park, B.H. Lee, S. Song, S.-J. Moon, S. Hwang, P.-O. Morin, M. Leclerc, G.M. Su, M.L. Chabinyc, H.Y. Woo, W.S. Shin, J.Y. Kim, High-efficiency photovoltaic cells with wide optical band gap polymers based on fluorinated phenylene-alkoxybenzothiadiazole, Energy Environ. Sci. 10 (2017) 1443–1455. https://doi.org/10.1039/C6EE03051C.
[186] J. Zhao, Y. Li, G. Yang, K. Jiang, H. Lin, H. Ade, W. Ma, H. Yan, Efficient organic solar cells processed from hydrocarbon solvents, Nat. Energy. 1 (2016) 15027. https://doi.org/10.1038/nenergy.2015.27.

[187] P.P. Khlyabich, B. Burkhart, C.F. Ng, B.C. Thompson, Efficient Solar Cells from Semi-random P3HT Analogues Incorporating Diketopyrrolopyrrole, Macromolecules. 44 (2011) 5079–5084. https://doi.org/10.1021/ma2009386.

[188] J.B. Howard, B.C. Thompson, Design of Random and Semi-Random Conjugated Polymers for Organic Solar Cells., Macromol. Chem. Phys. 218 (2017) 1700255. https://doi.org/10.1002/macp.201700255.

[189] H.J. Cho, Y.J. Kim, S. Chen, J. Lee, T.J. Shin, C.E. Park, C. Yang, Over 10% efficiency in single-junction polymer solar cells developed from easily accessible random terpolymers, Nano Energy. 39 (2017) 229–237. https://doi.org/10.1016/j.nanoen.2017.06.051.

[190] S.H. Park, S. Park, D. Kurniawan, J.G. Son, J.H. Noh, H. Ahn, H.J. Son, Highly Efficient Large-Area Organic Photovoltaic Module with a 350 nm Thick Active Layer Using a Random Terpolymer Donor, Chem. Mater. (2020). https://doi.org/10.1021/acs.chemmater.9b05399.

[191] R.M. Pankow, N.S. Gobalasingham, J.D. Munteanu, B.C. Thompson, Preparation of semi-alternating conjugated polymers using direct arylation polymerization (DArP) and improvement of photovoltaic device performance through structural variation, J. Polym. Sci. Part A: Polym. Chem. 55 (2017) 3370–3380. https://doi.org/10.1002/pola.28712.

[192] H. Yao, Y. Cui, D. Qian, C.S. Ponseca, A. Honarfar, Y. Xu, J. Xin, Z. Chen, L. Hong, B. Gao, R. Yu, Y. Zu, W. Ma, P. Chabera, T. Pullerits, A. Yartsev, F. Gao, J. Hou, 14.7% Efficiency Organic Photovoltaic Cells Enabled by Active Materials with a Large Electrostatic Potential Difference, J. Am. Chem. Soc. 141 (2019) 7743–7750. https://doi.org/10.1021/jacs.8b12937.

[193] S.J. Jeon, Y.W. Han, D.K. Moon, Chlorine Effects of Heterocyclic Ring-Based Donor Polymer for Low-Cost and High-Performance Nonfullerene Polymer Solar Cells, Solar RRL. 3 (2019) 1900094. https://doi.org/10.1002/solr.201900094.

[194] D. Dang, D. Yu, E. Wang, Conjugated Donor–Acceptor Terpolymers Toward High-Efficiency Polymer Solar Cells, Advanced Materials. 31 (2019) 1807019. https://doi.org/10.1002/adma.201807019.

[195] T.E. Kang, K.-H. Kim, B.J. Kim, Design of terpolymers as electron donors for highly efficient polymer solar cells, J. Mater. Chem. A. 2 (2014) 15252–15267. https://doi.org/10.1039/C4TA02426E.

[196] Y. Cui, H. Yao, L. Hong, T. Zhang, Y. Xu, K. Xian, B. Gao, J. Qin, J. Zhang, Z. Wei, J. Hou, Achieving Over 15% Efficiency in Organic Photovoltaic Cells via Copolymer Design, Advanced Materials. 31 (2019) 1808356. https://doi.org/10.1002/adma.201808356.

[197] T.E. Kang, J. Choi, H.-H. Cho, S.C. Yoon, B.J. Kim, Donor–Acceptor Random versus Alternating Copolymers for Efficient Polymer Solar Cells: Importance of Optimal Composition in Random Copolymers, Macromolecules. 49 (2016) 2096–2105. https://doi.org/10.1021/acs.macromol.5b02772.

[198] N.S. Gobalasingham, B.C. Thompson, Direct Arylation Polymerization: A Guide to Optimal Conditions for Effective Conjugated Polymers, Progress in Polymer Science. 83 (2018) 135–201. https://doi.org/10.1016/j.progpolymsci.2018.06.002.

[199] J.-R. Pouliot, F. Grenier, J.T. Blaskovits, S. Beaupré, M. Leclerc, Direct (Hetero)arylation Polymerization: Simplicity for Conjugated Polymer Synthesis, Chem. Rev. 116 (2016) 14225–14274. https://doi.org/10.1021/acs.chemrev.6b00498.

[200] H. Bohra, M. Wang, Direct C–H arylation: a "Greener" approach towards facile synthesis of organic semiconducting molecules and polymers, Journal of Materials Chemistry A. 5 (2017) 11550–11571. https://doi.org/10.1039/C7TA00617A.

[201] R.M. Pankow, B.C. Thompson, Approaches for improving the sustainability of conjugated polymer synthesis using direct arylation polymerization (DArP), Polym. Chem. 11 (2020) 630–640. https://doi.org/10.1039/C9PY01534E.

[202] Facchetti Antonio, Vaccaro Luigi, Marrocchi Assunta, Semiconducting Polymers Prepared by Direct Arylation Polycondensation, Angewandte Chemie International Edition. 51 (2012) 3520–3523. https://doi.org/10.1002/anie.201200199.

[203] K. Okamoto, J. Zhang, J.B. Housekeeper, S.R. Marder, C.K. Luscombe, C–H Arylation Reaction: Atom Efficient and Greener Syntheses of π-Conjugated Small Molecules and Macromolecules for Organic Electronic Materials, Macromolecules. 46 (2013) 8059–8078. https://doi.org/10.1021/ma401190r.

[204] P. Berrouard, A. Najari, A. Pron, D. Gendron, P.-O. Morin, J.-R. Pouliot, J. Veilleux, M. Leclerc, Synthesis of 5-Alkyl[3,4-c]thienopyrrole-4,6-dione-Based Polymers by Direct Heteroarylation, Angew. Chem. Int. Ed. 51 (2012) 2068–2071. https://doi.org/10.1002/anie.201106411.

[205] W. Lu, J. Kuwabara, T. Kanbara, Synthesis of 4,4′-dinonyl-2,2′-bithiazole-based copolymers via Pd-catalyzed direct C–H arylation, Polym. Chem. 3 (2012) 3217–3219. https://doi.org/10.1039/C2PY20539D.

[206] W. Lu, J. Kuwabara, T. Iijima, H. Higashimura, H. Hayashi, T. Kanbara, Synthesis of π-Conjugated Polymers Containing Fluorinated Arylene Units via Direct Arylation: Efficient Synthetic Method of Materials for OLEDs, Macromolecules. 45 (2012) 4128–4133. https://doi.org/10.1021/ma3004899.

[207] L.-C. Campeau, D.R. Stuart, J.-P. Leclerc, M. Bertrand-Laperle, E. Villemure, H.-Y. Sun, S. Lasserre, N. Guimond, M. Lecavallier, K. Fagnou, Palladium-Catalyzed Direct Arylation of Azine and Azole N-Oxides: Reaction Development, Scope and Applications in Synthesis, J. Am. Chem. Soc. 131 (2009) 3291–3306. https://doi.org/10.1021/ja808332k.

[208] S.I. Gorelsky, D. Lapointe, K. Fagnou, Analysis of the Concerted Metalation-Deprotonation Mechanism in Palladium-Catalyzed Direct Arylation Across a Broad Range of Aromatic Substrates, J. Am. Chem. Soc. 130 (2008) 10848–10849. https://doi.org/10.1021/ja802533u.

[209] S.I. Gorelsky, D. Lapointe, K. Fagnou, Analysis of the Palladium-Catalyzed (Aromatic)C–H Bond Metalation–Deprotonation Mechanism Spanning the Entire Spectrum of Arenes, J. Org. Chem. 77 (2012) 658–668. https://doi.org/10.1021/jo202342q.

[210] M. Lafrance, K. Fagnou, Palladium-Catalyzed Benzene Arylation: Incorporation of Catalytic Pivalic Acid as a Proton Shuttle and a Key Element in Catalyst Design, J. Am. Chem. Soc. 128 (2006) 16496–16497.

[211] B. Liegault, D. Lapointe, L. Caron, A. Vlassova, Keith. Fagnou, Establishment of Broadly Applicable Reaction Conditions for the Palladium-Catalyzed Direct Arylation of Heteroatom-Containing Aromatic Compounds., J. Org. Chem. 74 (2009) 1826–1834. https://doi.org/10.1021/jo8026565.

[212] F. Lombeck, F. Marx, K. Strassel, S. Kunz, C. Lienert, H. Komber, R. Friend, M. Sommer, To branch or not to branch: C–H selectivity of thiophene-based donor–acceptor–donor monomers in direct arylation polycondensation exemplified by PCDTBT, Polym. Chem. 8 (2017) 4738–4745. https://doi.org/10.1039/C7PY00879A.

[213] A.S. Dudnik, T.J. Aldrich, N.D. Eastham, R.P.H. Chang, A. Facchetti, T.J. Marks, Tin-Free Direct C–H Arylation Polymerization for High Photovoltaic Efficiency Conjugated Copolymers, J. Am. Chem. Soc. 138 (2016) 15699–15709. https://doi.org/10.1021/jacs.6b10023.
[214] R. Matsidik, H. Komber, A. Luzio, M. Caironi, M. Sommer, Defect-free Naphthalene Diimide Bithiophene Copolymers with Controlled Molar Mass and High Performance via Direct Arylation Polycondensation, J. Am. Chem. Soc. 137 (2015) 6705–6711. https://doi.org/10.1021/jacs.5b03355.
[215] N.S. Gobalasingham, S. Ekiz, R.M. Pankow, F. Livi, E. Bundgaard, B.C. Thompson, Carbazole-based copolymers via direct arylation polymerization (DArP) for Suzuki-convergent polymer solar cell performance, Polym. Chem. 8 (2017) 4393–4402. https://doi.org/10.1039/C7PY00859G.
[216] N.S. Gobalasingham, R.M. Pankow, S. Ekiz, B.C. Thompson, Evaluating structure–function relationships toward three-component conjugated polymers via direct arylation polymerization (DArP) for Stille-convergent solar cell performance, J. Mater. Chem. A. 5 (2017) 14101–14113. https://doi.org/10.1039/C7TA03980H.
[217] F. Livi, N.S. Gobalasingham, B.C. Thompson, E. Bundgaard, Analysis of diverse direct arylation polymerization (DArP) conditions toward the efficient synthesis of polymers converging with stille polymers in organic solar cells, J. Polym. Sci., Part A. 54 (2016) 2907–2918. https://doi.org/10.1002/pola.28176.
[218] L. Ye, R.M. Pankow, M. Horikawa, E.L. Melenbrink, K. Liu, B.C. Thompson, Green Solvent Processed Amide-Functionalized Conjugated Poly-mers Prepared via Direct Arylation Polymerization (DArP), Macromolecules. 52 (2019) 9383–9388. https://doi.org/10.1021/acs.macromol.9b02014.
[219] R.M. Pankow, L. Ye, B.C. Thompson, Copper catalyzed synthesis of conjugated copolymers using direct arylation polymerization, Polym. Chem. 9 (2018) 4120–4124. https://doi.org/10.1039/C8PY00913A.
[220] R.M. Pankow, L. Ye, B.C. Thompson, Sustainable Synthesis of a Fluorinated Arylene Conjugated Polymer via Cu-Catalyzed Direct Arylation Polymerization (DArP), ACS Macro Lett. 7 (2018) 1232–1236. https://doi.org/10.1021/acsmacrolett.8b00618.
[221] L. Ye, R.M. Pankow, A. Schmitt, B.C. Thompson, Synthesis of Conjugated Polymers using Aryl-Bromides via Cu-Catalyzed Direct Arylation Polymerization (Cu-DArP), Polymer Chemistry. in revision (2019).
[222] N.S. Gobalasingham, S. Noh, B.C. Thompson, Palladium-catalyzed oxidative direct arylation polymerization (Oxi-DArP) of an ester-functionalized thiophene, Polym. Chem. 7 (2016) 1623–1631. https://doi.org/10.1039/C5PY01973G.
[223] N.S. Gobalasingham, R.M. Pankow, B.C. Thompson, Synthesis of random poly(hexyl thiophene-3-carboxylate) copolymers via oxidative direct arylation polymerization (oxi-DArP), Polym. Chem. 8 (2017) 1963–1971. https://doi.org/10.1039/C7PY00181A.
[224] A. Faradhiyani, Q. Zhang, K. Maruyama, J. Kuwabara, T. Yasuda, T. Kanbara, Synthesis of bithiazole-based semiconducting polymers via Cu-catalysed aerobic oxidative coupling, Mater. Chem. Front. 2 (2018) 1306–1309. https://doi.org/10.1039/C7QM00584A.
[225] G.S. Collier, J.R. Reynolds, Exploring the Utility of Buchwald Ligands for C–H Oxidative Direct Arylation Polymerizations, ACS Macro Lett. 8 (2019) 931–936. https://doi.org/10.1021/acsmacrolett.9b00395.

[226] H. Aoki, H. Saito, Y. Shimoyama, J. Kuwabara, T. Yasuda, T. Kanbara, Synthesis of Conjugated Polymers Containing Octafluorobiphenylene Unit via Pd-Catalyzed Cross-Dehydrogenative-Coupling Reaction, ACS Macro Lett. (2017) 90–94. https://doi.org/10.1021/acsmacrolett.7b00887.

[227] Q. Zhang, M. Chang, Y. Lu, Y. Sun, C. Li, X. Yang, M. Zhang, Y. Chen, A Direct C–H Coupling Method for Preparing π-Conjugated Functional Polymers with High Regioregularity, Macromolecules. 51 (2018) 379–388. https://doi.org/10.1021/acs.macromol.7b02390.

[228] J. Xiang, C.-L. Ho, W.-Yeung. Wong, Metallopolymers for energy production, storage and conservation., Polym. Chem. 6 (2015) 6905–6930. https://doi.org/10.1039/C5PY00941C.

[229] C. Dai, B. Liu, Conjugated polymers for visible-light-driven photocatalysis, Energy Environ. Sci. 13 (2020) 24–52. https://doi.org/10.1039/C9EE01935A.

[230] S.E. Root, S. Savagatrup, A.D. Printz, D. Rodriquez, D.J. Lipomi, Mechanical properties of organic semiconductors for stretchable, highly flexible, and mechanically robust electronics., Chem. Rev. (Washington, DC, U. S.). 117 (2017) 6467–6499. https://doi.org/10.1021/acs.chemrev.7b00003.

[231] E.L. Melenbrink, K.M. Hilby, M.A. Alkhadra, S. Samal, D.J. Lipomi, B.C. Thompson, Influence of Systematic Incorporation of Conjugation-Break Spacers into Semi-Random Polymers on Mechanical and Electronic Properties, ACS Appl. Mater. Interfaces. (2018). https://doi.org/10.1021/acsami.8b10608.

[232] M. Jørgensen, K. Norrman, S.A. Gevorgyan, T. Tromholt, B. Andreasen, F.C. Krebs, Stability of Polymer Solar Cells, Adv. Mater. 24 (2012) 580–612. https://doi.org/10.1002/adma.201104187.

[233] M. Manceau, E. Bundgaard, J.E. Carlé, O. Hagemann, M. Helgesen, R. Søndergaard, M. Jørgensen, F.C. Krebs, Photochemical stability of π-conjugated polymers for polymer solar cells: a rule of thumb, J. Mater. Chem. 21 (2011) 4132–4141. https://doi.org/10.1039/C0JM03105D.

[234] K. Wang, Y. Li, Y. Li, Challenges to the Stability of Active Layer Materials in Organic Solar Cells, Macromolecular Rapid Communications. 41 (2020) 1900437. https://doi.org/10.1002/marc.201900437.

[235] M. Manceau, A. Rivaton, J.-L. Gardette, S. Guillerez, N. Lemaître, The mechanism of photo- and thermooxidation of poly(3-hexylthiophene) (P3HT) reconsidered, Polymer Degradation and Stability. 94 (2009) 898–907. https://doi.org/10.1016/j.polymdegradstab.2009.03.005.

[236] M. Manceau, A. Rivaton, J.-L. Gardette, Involvement of Singlet Oxygen in the Solid-State Photochemistry of P3HT, Macromolecular Rapid Communications. 29 (2008) 1823–1827. https://doi.org/10.1002/marc.200800421.

[237] O.R. Yamilova, I.V. Martynov, A.S. Brandvold, I.V. Klimovich, A.H. Balzer, A.V. Akkuratov, I.E. Kusnetsov, N. Stingelin, P.A. Troshin, What is Killing Organic Photovoltaics: Light-Induced Crosslinking as a General Degradation Pathway of Organic Conjugated Molecules, Advanced Energy Materials. 10 (2020) 1903163. https://doi.org/10.1002/aenm.201903163.

[238] C.-N. Weng, H.-C. Yang, C.-Y. Tsai, S.-H. Chen, Y.-S. Chen, C.-H. Chen, K.-M. Huang, H.-F. Meng, Y.-C. Chao, C.-Y. Chang, H.-W. Zan, S.-F. Horng, P.-C. Yu, K.-W. Su, The influence of UV filter and Al/Ag moisture barrier layer on the outdoor stability of polymer solar cells, Solar Energy. 199 (2020) 308–316. https://doi.org/10.1016/j.solener.2020.02.041.

[239] M. Karakawa, K. Suzuki, T. Kuwabara, T. Taima, K. Nagai, M. Nakano, T. Yamaguchi, K. Takahashi, Factors contributing to degradation of organic photovoltaic cells, Organic Electronics. 76 (2020) 105448. https://doi.org/10.1016/j.orgel.2019.105448.
[240] C. Lee, J. Lee, S. Lee, W. Lee, H. You, H.Y. Woo, B.J. Kim, Importance of device structure and interlayer design in storage stability of naphthalene diimide-based all-polymer solar cells, J. Mater. Chem. A. 8 (2020) 3735–3745. https://doi.org/10.1039/C9TA14032H.
[241] S. Rafique, S.M. Abdullah, K. Sulaiman, M. Iwamoto, Fundamentals of bulk heterojunction organic solar cells: An overview of stability/degradation issues and strategies for improvement, Renewable and Sustainable Energy Reviews. 84 (2018) 43–53. https://doi.org/10.1016/j.rser.2017.12.008.
[242] W.R. Mateker, M.D. McGehee, Progress in Understanding Degradation Mechanisms and Improving Stability in Organic Photovoltaics, Advanced Materials. 29 (2017) 1603940. https://doi.org/10.1002/adma.201603940.
[243] A. Tournebize, J.-L. Gardette, C. Taviot-Guého, D. Bégué, M.A. Arnaud, C. Dagron-Lartigau, H. Medlej, R.C. Hiorns, S. Beaupré, M. Leclerc, A. Rivaton, Is there a photostable conjugated polymer for efficient solar cells?, Polymer Degradation and Stability. 112 (2015) 175–184. https://doi.org/10.1016/j.polymdegradstab.2014.12.018.
[244] S. Kim, M.A.M. Rashid, T. Ko, K. Ahn, Y. Shin, S. Nah, M.H. Kim, B. Kim, K. Kwak, M. Cho, New Insights into the Photodegradation Mechanism of the PTB7-Th Film: Photooxidation of π-Conjugated Backbone upon Sunlight Illumination, J. Phys. Chem. C. 124 (2020) 2762–2770. https://doi.org/10.1021/acs.jpcc.9b09954.
[245] E.M. Speller, A.J. Clarke, N. Aristidou, M.F. Wyatt, L. Francàs, G. Fish, H. Cha, H.K.H. Lee, J. Luke, A. Wadsworth, A.D. Evans, I. McCulloch, J.-S. Kim, S.A. Haque, J.R. Durrant, S.D. Dimitrov, W.C. Tsoi, Z. Li, Toward Improved Environmental Stability of Polymer:Fullerene and Polymer:Nonfullerene Organic Solar Cells: A Common Energetic Origin of Light- and Oxygen-Induced Degradation, ACS Energy Lett. (2019) 846–852. https://doi.org/10.1021/acsenergylett.9b00109.
[246] J.Y. Oh, S. Rondeau-Gagné, Y.-C. Chiu, A. Chortos, F. Lissel, G.-J.N. Wang, B.C. Schroeder, T. Kurosawa, J. Lopez, T. Katsumata, J. Xu, C. Zhu, X. Gu, W.-G. Bae, Y. Kim, L. Jin, J.W. Chung, J.B.-H. Tok, Z. Bao, Intrinsically stretchable and healable semiconducting polymer for organic transistors, Nature. 539 (2016) 411–415. https://doi.org/10.1038/nature20102.
[247] C. Liao, M. Zhang, M.Y. Yao, T. Hua, L. Li, F. Yan, Flexible Organic Electronics in Biology: Materials and Devices, Advanced Materials. 27 (2015) 7493–7527. https://doi.org/10.1002/adma.201402625.
[248] B. Roth, S. Savagatrup, N. V. de los Santos, O. Hagemann, J.E. Carlé, M. Helgesen, F. Livi, E. Bundgaard, R.R. Søndergaard, F.C. Krebs, D.J. Lipomi, Mechanical Properties of a Library of Low-Band-Gap Polymers, Chem. Mater. 28 (2016) 2363–2373. https://doi.org/10.1021/acs.chemmater.6b00525.
[249] B. Wang, A. Facchetti, Mechanically Flexible Conductors for Stretchable and Wearable E-Skin and E-Textile Devices, Advanced Materials. 31 (2019) 1901408. https://doi.org/10.1002/adma.201901408.
[250] Y. Zhao, X. Zhao, Y. Zang, C. Di, Y. Diao, J. Mei, Conjugation-Break Spacers in Semiconducting Polymers: Impact on Polymer Processability and Charge Transport Properties, Macromolecules. 48 (2015) 2048–2053. https://doi.org/10.1021/acs.macromol.5b00194.

[251] A. Gasperini, S. Bivaud, K. Sivula, Controlling conjugated polymer morphology and charge carrier transport with a flexible-linker approach, Chem. Sci. 5 (2014) 4922–4927. https://doi.org/10.1039/C4SC02073A.
[252] X. Zhao, G. Xue, G. Qu, V. Singhania, Y. Zhao, K. Butrouna, A. Gumyusenge, Y. Diao, K.R. Graham, H. Li, J. Mei, Complementary Semiconducting Polymer Blends: Influence of Side Chains of Matrix Polymers, Macromolecules. 50 (2017) 6202–6209. https://doi.org/10.1021/acs.macromol.7b01354.
[253] J. Mei, D.H. Kim, A.L. Ayzner, M.F. Toney, Z. Bao, Siloxane-Terminated Solubilizing Side Chains: Bringing Conjugated Polymer Backbones Closer and Boosting Hole Mobilities in Thin-Film Transistors, J. Am. Chem. Soc. 133 (2011) 20130–20133. https://doi.org/10.1021/ja209328m.
[254] S. Savagatrup, X. Zhao, E. Chan, J. Mei, D.J. Lipomi, Effect of Broken Conjugation on the Stretchability of Semiconducting Polymers, Macromolecular Rapid Communications. 37 (2016) 1623–1628. https://doi.org/10.1002/marc.201600377.
[255] Y. Cui, H. Yao, J. Zhang, K. Xian, T. Zhang, L. Hong, Y. Wang, Y. Xu, K. Ma, C. An, C. He, Z. Wei, F. Gao, J. Hou, Single-Junction Organic Photovoltaic Cells with Approaching 18% Efficiency, Advanced Materials. n/a (2020) 1908205. https://doi.org/10.1002/adma.201908205.
[256] C.-J. Yang, S.A. Jenekhe, Conjugated Aromatic Polyimines. 2. Synthesis, Structure, and Properties of New Aromatic Polyazomethines, Macromolecules. 28 (1995) 1180–1196. https://doi.org/10.1021/ma00108a054.
[257] S. Barik, W.G. Skene, Turning-on the Quenched Fluorescence of Azomethines through Structural Modifications., Eur. J. Org. Chem. 2013 (2013) 2563–2572. https://doi.org/10.1002/ejoc.201201502.
[258] S. Barik, W.G. Skene, A fluorescent all-fluorene polyazomethine - towards soluble conjugated polymers exhibiting high fluorescence and electrochromic properties., Polym. Chem. 2 (2011) 1091–1097. https://doi.org/10.1039/c0py00394h.
[259] S. Barik, D. Navarathne, M. LeBorgne, W.G. Skene, Conjugated thiophenoazomethines: electrochromic materials exhibiting visible-to-near-IR color changes., J. Mater. Chem. C. 1 (2013) 5508–5519. https://doi.org/10.1039/c3tc30494a.
[260] A. Bolduc, S. Barik, M.R. Lenze, K. Meerholz, W.G. Skene, Polythiophenoazomethines - alternate photoactive materials for organic photovoltaics., J. Mater. Chem. A. 2 (2014) 15620–15626. https://doi.org/10.1039/C4TA03202K.
[261] K.K. Fu, Z. Wang, J. Dai, M. Carter, Liangbing. Hu, Transient Electronics: Materials and Devices., Chem. Mater. (2016) Ahead of Print. https://doi.org/10.1021/acs.chemmater.5b04931.
[262] S.-K. Kang, J. Koo, Y.K. Lee, J.A. Rogers, Advanced Materials and Devices for Bioresorbable Electronics, Acc. Chem. Res. 51 (2018) 988–998. https://doi.org/10.1021/acs.accounts.7b00548.
[263] M. Kuzma, E. Gerhard, D. Shan, J. Yang, Advances in Bioresorbable Electronics and Uses in Biomedical Sensing, in: H. Cao, T. Coleman, T.K. Hsiai, A. Khademhosseini (Eds.), Interfacing Bioelectronics and Biomedical Sensing, Springer International Publishing, Cham, 2020: pp. 29–72. https://doi.org/10.1007/978-3-030-34467-2_2.
[264] C.J. Bettinger, Z. Bao, Organic Thin-Film Transistors Fabricated on Resorbable Biomaterial Substrates, Advanced Materials. 22 (2010) 651–655. https://doi.org/10.1002/adma.200902322.

[265] C.J. Bettinger, Advances in Materials and Structures for Ingestible Electromechanical Medical Devices, Angewandte Chemie International Edition. 57 (2018) 16946–16958. https://doi.org/10.1002/anie.201806470.
[266] T. Lei, M. Guan, J. Liu, H.-C. Lin, R. Pfattner, L. Shaw, A.F. McGuire, T.-C. Huang, L. Shao, K.-T. Cheng, J.B.-H. Tok, Z. Bao, Biocompatible and totally disintegrable semiconducting polymer for ultrathin and ultralightweight transient electronics, Proc Natl Acad Sci USA. 114 (2017) 5107. https://doi.org/10.1073/pnas.1701478114.
[267] J. Roncali, I. Grosu, The Dawn of Single Material Organic Solar Cells, Advanced Science. 6 (2019) 1801026. https://doi.org/10.1002/advs.201801026.
[268] M. Sommer, S. Huettner, M. Thelakkat, Donor–acceptor block copolymers for photovoltaic applications, J. Mater. Chem. 20 (2010) 10788–10797. https://doi.org/10.1039/C0JM00665C.
[269] J. Roncali, Single Material Solar Cells: the Next Frontier for Organic Photovoltaics?, Advanced Energy Materials. 1 (2011) 147–160. https://doi.org/10.1002/aenm.201000008.
[270] J. Roncali, Linear π-conjugated systems derivatized with C60-fullerene as molecular heterojunctions for organic photovoltaics, Chem. Soc. Rev. 34 (2005) 483–495. https://doi.org/10.1039/B415941C.
[271] F. Pierini, M. Lanzi, P. Nakielski, S. Pawłowska, O. Urbanek, K. Zembrzycki, T.A. Kowalewski, Single-Material Organic Solar Cells Based on Electrospun Fullerene-Grafted Polythiophene Nanofibers, Macromolecules. 50 (2017) 4972–4981. https://doi.org/10.1021/acs.macromol.7b00857.
[272] G. Feng, J. Li, F.J.M. Colberts, M. Li, J. Zhang, F. Yang, Y. Jin, F. Zhang, R.A.J. Janssen, C. Li, W. Li, “Double-Cable” Conjugated Polymers with Linear Backbone toward High Quantum Efficiencies in Single-Component Polymer Solar Cells, J. Am. Chem. Soc. 139 (2017) 18647–18656. https://doi.org/10.1021/jacs.7b10499.
[273] J.H. Lee, C.G. Park, A. Kim, H.J. Kim, Y. Kim, S. Park, M.J. Cho, D.H. Choi, High-Performance Polymer Solar Cell with Single Active Material of Fully Conjugated Block Copolymer Composed of Wide-Band gap Donor and Narrow-Band gap Acceptor Blocks, ACS Appl. Mater. Interfaces. 10 (2018) 18974–18983. https://doi.org/10.1021/acsami.8b03580.
[274] J. Chung, A. Khot, B.M. Savoie, B.W. Boudouris, 100th Anniversary of Macromolecular Science Viewpoint: Recent Advances and Opportunities for Mixed Ion and Charge Conducting Polymers, ACS Macro Lett. (2020) 646–655. https://doi.org/10.1021/acsmacrolett.0c00037.
[275] F. Zhao, Y. Shi, L. Pan, G. Yu, Multifunctional Nanostructured Conductive Polymer Gels: Synthesis, Properties, and Applications, Acc. Chem. Res. 50 (2017) 1734–1743. https://doi.org/10.1021/acs.accounts.7b00191.
[276] M. Goel, C.D. Heinrich, G. Krauss, M. Thelakkat, Principles of Structural Design of Conjugated Polymers Showing Excellent Charge Transport toward Thermoelectrics and Bioelectronics Applications, Macromolecular Rapid Communications. 40 (2019) 1800915. https://doi.org/10.1002/marc.201800915.
[277] B.D. Paulsen, K. Tybrandt, E. Stavrinidou, J. Rivnay, Organic mixed ionic–electronic conductors, Nature Materials. 19 (2020) 13–26. https://doi.org/10.1038/s41563-019-0435-z.
[278] J. Rivnay, S. Inal, A. Salleo, R.M. Owens, M. Berggren, G.G. Malliaras, Organic electrochemical transistors, Nature Reviews Materials. 3 (2018) 17086. https://doi.org/10.1038/natrevmats.2017.86.

[279] C.-H. Lai, D.S. Ashby, T.C. Lin, J. Lau, A. Dawson, S.H. Tolbert, B.S. Dunn, Application of Poly(3-hexylthiophene-2,5-diyl) as a Protective Coating for High Rate Cathode Materials, Chem. Mater. 30 (2018) 2589–2599. https://doi.org/10.1021/acs.chemmater.7b05116.

[280] C.G. Bischak, L.Q. Flagg, K. Yan, T. Rehman, D.W. Davies, R.J. Quezada, J.W. Onorato, C.K. Luscombe, Y. Diao, C.-Z. Li, D.S. Ginger, A Reversible Structural Phase Transition by Electrochemically-Driven Ion Injection into a Conjugated Polymer, J. Am. Chem. Soc. 142 (2020) 7434–7442. https://doi.org/10.1021/jacs.9b12769.

[281] L.R. Savagian, A.M. Österholm, J.F. Ponder Jr., K.J. Barth, J. Rivnay, J.R. Reynolds, Balancing Charge Storage and Mobility in an Oligo(Ether) Functionalized Dioxythiophene Copolymer for Organic- and Aqueous- Based Electrochemical Devices and Transistors, Advanced Materials. 30 (2018) 1804647. https://doi.org/10.1002/adma.201804647.

[282] S. Inal, J. Rivnay, P. Leleux, M. Ferro, M. Ramuz, J.C. Brendel, M.M. Schmidt, M. Thelakkat, G.G. Malliaras, A High Transconductance Accumulation Mode Electrochemical Transistor, Advanced Materials. 26 (2014) 7450–7455. https://doi.org/10.1002/adma.201403150.

[283] A. Giovannitti, D.-T. Sbircea, S. Inal, C.B. Nielsen, E. Bandiello, D.A. Hanifi, M. Sessolo, G.G. Malliaras, I. McCulloch, J. Rivnay, Controlling the mode of operation of organic transistors through side-chain engineering, Proc Natl Acad Sci USA. 113 (2016) 12017. https://doi.org/10.1073/pnas.1608780113.

[284] D. Kiefer, A. Giovannitti, H. Sun, T. Biskup, A. Hofmann, M. Koopmans, C. Cendra, S. Weber, L.J. Anton Koster, E. Olsson, J. Rivnay, S. Fabiano, I. McCulloch, C. Müller, Enhanced n-Doping Efficiency of a Naphthalenediimide-Based Copolymer through Polar Side Chains for Organic Thermoelectrics, ACS Energy Lett. 3 (2018) 278–285. https://doi.org/10.1021/acsenergylett.7b01146.

[285] X. Chen, S. Shen, L. Guo, S.S. Mao, Semiconductor-based Photocatalytic Hydrogen Generation, Chem. Rev. 110 (2010) 6503–6570. https://doi.org/10.1021/cr1001645.

[286] L. Shi, W. Xia, Photoredox functionalization of C–H bonds adjacent to a nitrogen atom, Chem. Soc. Rev. 41 (2012) 7687–7697. https://doi.org/10.1039/C2CS35203F.

[287] T. Hisatomi, J. Kubota, K. Domen, Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting, Chem. Soc. Rev. 43 (2014) 7520–7535. https://doi.org/10.1039/C3CS60378D.

[288] J. Willkomm, K.L. Orchard, A. Reynal, E. Pastor, J.R. Durrant, E. Reisner, Dye-sensitised semiconductors modified with molecular catalysts for light-driven H2 production, Chem. Soc. Rev. 45 (2016) 9–23. https://doi.org/10.1039/C5CS00733J.

[289] Z. Hu, Z. Wang, X. Zhang, H. Tang, X. Liu, F. Huang, Y. Cao, Conjugated Polymers with Oligoethylene Glycol Side Chains for Improved Photocatalytic Hydrogen Evolution, IScience. 13 (2019) 33–42. https://doi.org/10.1016/j.isci.2019.02.007.

[290] C. Dai, M. Panahandeh-Fard, X. Gong, C. Xue, B. Liu, Water-Dispersed Conjugated Polyelectrolyte for Visible-Light Hydrogen Production, Solar RRL. 3 (2019) 1800255. https://doi.org/10.1002/solr.201800255.

[291] P.B. Pati, G. Damas, L. Tian, D.L.A. Fernandes, L. Zhang, I.B. Pehlivan, T. Edvinsson, C.M. Araujo, H. Tian, An experimental and theoretical study of an efficient polymer nano-photocatalyst for hydrogen evolution, Energy Environ. Sci. 10 (2017) 1372–1376. https://doi.org/10.1039/C7EE00751E.

[292] S. Yanagida, A. Kabumoto, K. Mizumoto, C. Pac, K. Yoshino, Poly(p-phenylene)-catalysed photoreduction of water to hydrogen, J. Chem. Soc., Chem. Commun. (1985) 474–475. https://doi.org/10.1039/C39850000474.

[293] Y. Lv, P. Liu, H. Ding, Y. Wu, Y. Yan, H. Liu, X. Wang, F. Huang, Y. Zhao, Z. Tian, Conjugated Polymer-Based Hybrid Nanoparticles with Two-Photon Excitation and Near-Infrared Emission Features for Fluorescence Bioimaging within the Biological Window, ACS Appl. Mater. Interfaces. 7 (2015) 20640–20648. https://doi.org/10.1021/acsami.5b05150.

[294] Y. Wang, B. Liu, A. Mikhailovsky, G.C. Bazan, Conjugated Polyelectrolyte–Metal Nanoparticle Platforms for Optically Amplified DNA Detection, Advanced Materials. 22 (2010) 656–659. https://doi.org/10.1002/adma.200902675.

[295] W. Wu, G. Feng, S. Xu, B. Liu, A Photostable Far-Red/Near-Infrared Conjugated Polymer Photosensitizer with Aggregation-Induced Emission for Image-Guided Cancer Cell Ablation, Macromolecules. 49 (2016) 5017–5025. https://doi.org/10.1021/acs.macromol.6b00958.

[296] W. Wu, G.C. Bazan, Bin. Liu, Conjugated-Polymer-Amplified Sensing, Imaging, and Therapy., Chem. 2 (2017) 760–790. https://doi.org/10.1016/j.chempr.2017.05.002.

[297] C. Zhu, L. Liu, Q. Yang, F. Lv, S. Wang, Water-Soluble Conjugated Polymers for Imaging, Diagnosis, and Therapy, Chem. Rev. 112 (2012) 4687–4735. https://doi.org/10.1021/cr200263w.

[298] G. Feng, D. Ding, B. Liu, Fluorescence bioimaging with conjugated polyelectrolytes, Nanoscale. 4 (2012) 6150–6165. https://doi.org/10.1039/C2NR31392H.

[299] S.W. Thomas, G.D. Joly, T.M. Swager, Chemical Sensors Based on Amplifying Fluorescent Conjugated Polymers, Chem. Rev. 107 (2007) 1339–1386. https://doi.org/10.1021/cr0501339.

[300] C. Wu, C. Szymanski, Z. Cain, J. McNeill, Conjugated Polymer Dots for Multiphoton Fluorescence Imaging, J. Am. Chem. Soc. 129 (2007) 12904–12905. https://doi.org/10.1021/ja074590d.

[301] J. Shi, Y. Wu, B. Tong, J. Zhi, Y. Dong, Tunable fluorescence upon aggregation: Photophysical properties of cationic conjugated polyelectrolytes containing AIE and ACQ units and their use in the dual-channel quantification of heparin, Sensors and Actuators B: Chemical. 197 (2014) 334–341. https://doi.org/10.1016/j.snb.2014.03.004.

[302] W. Wu, S. Ye, R. Tang, L. Huang, Q. Li, G. Yu, Y. Liu, J. Qin, Z. Li, New tetraphenylethylene-containing conjugated polymers: Facile synthesis, aggregation-induced emission enhanced characteristics and application as explosive chemsensors and PLEDs, Polymer. 53 (2012) 3163–3171. https://doi.org/10.1016/j.polymer.2012.05.035.

[303] Q. Zhang, H. Kuwabara, W.J. Potscavage, S. Huang, Y. Hatae, T. Shibata, C. Adachi, Anthraquinone-Based Intramolecular Charge-Transfer Compounds: Computational Molecular Design, Thermally Activated Delayed Fluorescence, and Highly Efficient Red Electroluminescence, J. Am. Chem. Soc. 136 (2014) 18070–18081. https://doi.org/10.1021/ja510144h.