



## Review

# Synthesizing optoelectronic heteroaromatic conjugated polymers by cross-coupling reactions

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## Abstract

Heteroaromatics-containing polymers comprise a huge class of materials that have received considerable attention due to their interesting electrical, electrochemical, and optical properties. In this review, the recent advances on the use of organometallic cross-coupling reactions for the synthesis of heteroaromatic conjugated polymers for the optoelectronic interests and applications are summarised.

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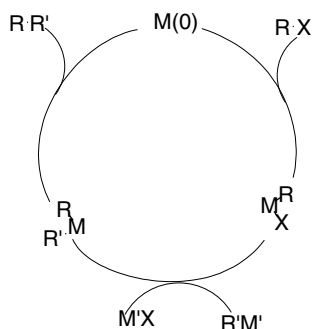
## 1. Introduction

Over the past two decades conducting polymers have received widespread attention due to their high conductivity and interesting optoelectronic properties [1]. The nature of conjugated system, the conjugation length, regio-regularity and the substituent(s), inter alia, may determine the performance of these polymers. In general, incorporation of heteroaromatic rings in these polymers has shown remarkable modification of the photophysical and electronic properties of these polymers [2]. Oxidative polymerization of heteroaromatic rings have been extensively used in the synthesis of these polymers. For example, heteroaromatic ring-containing polyaryls such as polypyrrole can be obtained by the electrochemical oxidation of the corresponding monomeric unit [3]. However, this process suffers from the gross defect that the structure of the polymer is somewhat undirected and undefined. X-ray photoemission studies indicate that as many as one in three pyrrole

rings is affected by structural disorder, part of which is attributed to non- $\alpha$ - $\alpha'$ -linkages [4]. The situation in which two linked aromatic units are electrochemically polymerized has been shown to be considerably worse [5]. Other oxidative polymerization [6], or Friedel-Crafts polymerization [7] processes give no control of linkage position or the degree of branching or cross-linking. Although polyphenylenes and the like can be obtained by the dehalogenation of the haloaromatic compounds with alkali metals (Wurtz–Fittig reaction) [8], the reaction normally requires high temperature and the polymers prepared may have some steric irregularities or branching due to the radical nature of the conventional coupling reactions.

Thanks to the rapid growth in the application of organometallic catalysts or reagents [9,10], conjugated polymers of a wide range of fascinating structural variety and regio-regularity have been synthesized. Moreover, the monomeric units are occasionally synthesized via transition metal catalyzed reactions. This review summarizes recent development in the synthesis of heteroaromatic conjugated polymers. Particular attention will be focused on the use of organometallic catalyst or reagent for the synthesis of these polymers. No

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Scheme 1.

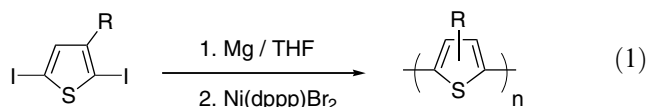
comprehensive coverage is attempted and only representative examples are summarized.

Transition metal catalyzed cross-coupling reaction provides a particularly powerful arsenal for the  $C_{sp^2}$ – $C_{sp^2}$  and  $C_{sp}$ – $C_{sp^2}$  bond formation [10]. More recently, alkyl halides or related unactivated electrophiles can also proceed smoothly [11,12]. The reaction in general involves the transition metal catalyzed oxidative addition reaction across the C–X bond of an electrophile, transmetalation with a main group organometallic nucleophile, followed by reductive elimination step leading to carbon–carbon bond formation and the active catalyst is regenerated (Scheme 1). Most commonly employed transition metal catalysts are nickel or palladium-based complexes, although other metals have also be used. The organometallic nucleophiles can be Grignard reagents (Kumada–Corriu), stannanes (Stille), boron reagents (Suzuki–Miyaura), lithium, copper, mercury, or zinc compounds.

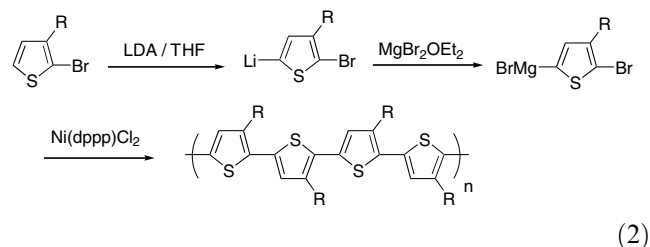
Conjugation length can thus be extended by means of this transformation and the application to polymer synthesis abounds. When the electrophilic and nucleophilic centers of the monomeric substrates are readily accessible, the regio-regularity of the polymers can be easily achieved.

## 2. Kumada–Corriu coupling

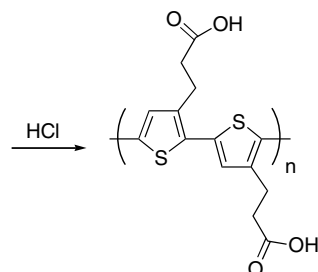
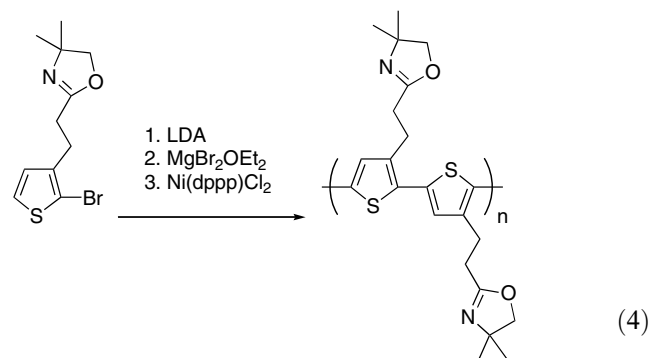
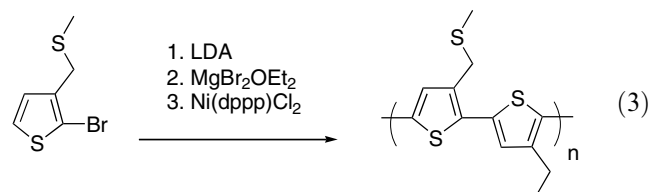
Poly(3-alkylthiophenes) are prepared by nickel-catalyzed Grignard couplings of the diiodothiophenes having alkyl at  $C_3$  position (Eq. (1)). Apparently, one of the C–I bond may react with magnesium to form the Grignard reagent which undergoes further coupling reaction. The reaction is simple but the regio-regularity can not be controlled. The deep red-colored polymers can be soluble in various organic solvents and show high conductivity after doping with acceptor dopants such as  $NOSbF_6$ ,  $FeCl_3$  or  $I_2$  [13].

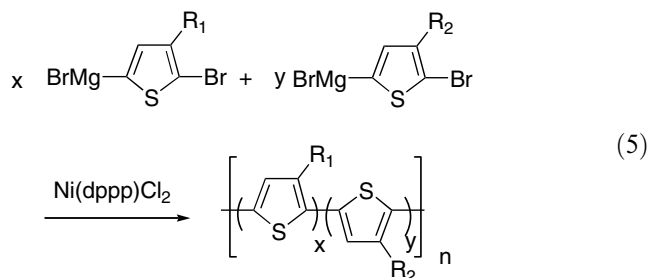


Regio-regular polymerization of 3-alkylthiophenes can be controlled by regioselective lithiation of 2-bromo-3-alkylthiophene with lithium diisopropylamide (LDA) followed by transmetalation with magnesium bromide to yield the organomagnesium intermediate. The use of  $NiCl_2(dppe)$  catalyst for the polymerization of this intermediate gives the corresponding polythiophene in over 90% of head-to-tail regioselectivity (Eq. (2)) [14].

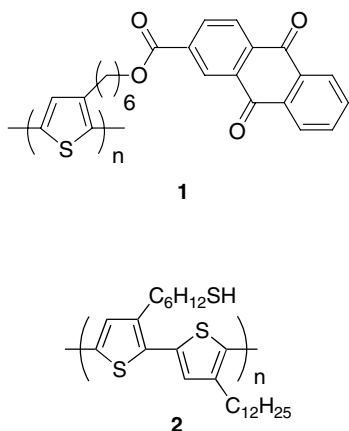


The regio-regularity of the poly(3-alkylthiophene-diyl)s obtained from this cross-coupling reaction appears to be much better than the polymer from electrochemical oxidation [15] or  $FeCl_3$  oxidation [16]. Polythiophenes with etheral side chain (Eq. (3)) [17], carboxylic acid group (Eq. (4)) [18] and copolymers of random head-to-tail regioselectivity (Eq. (5)) [19] are also obtained in a similar manner.

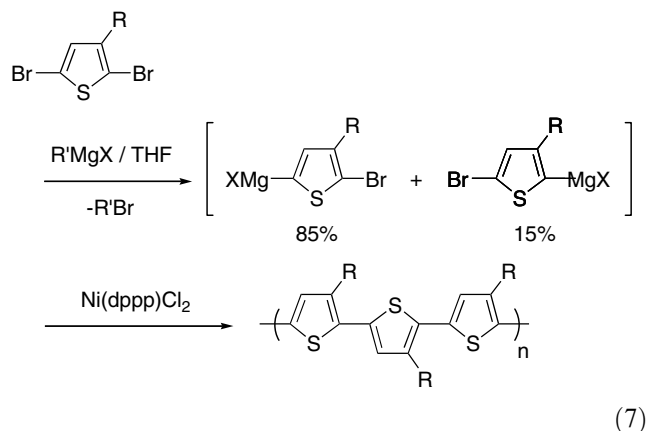
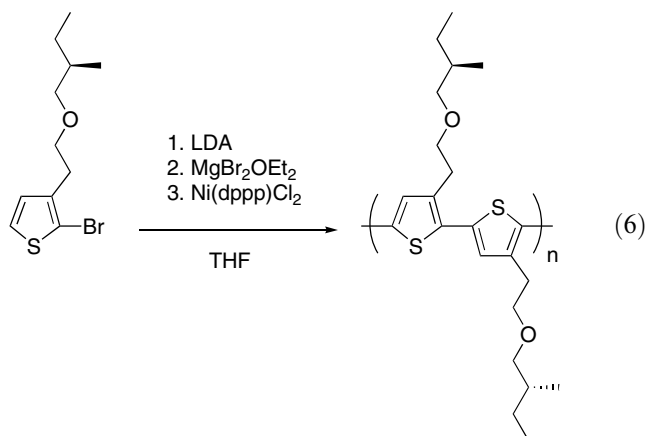




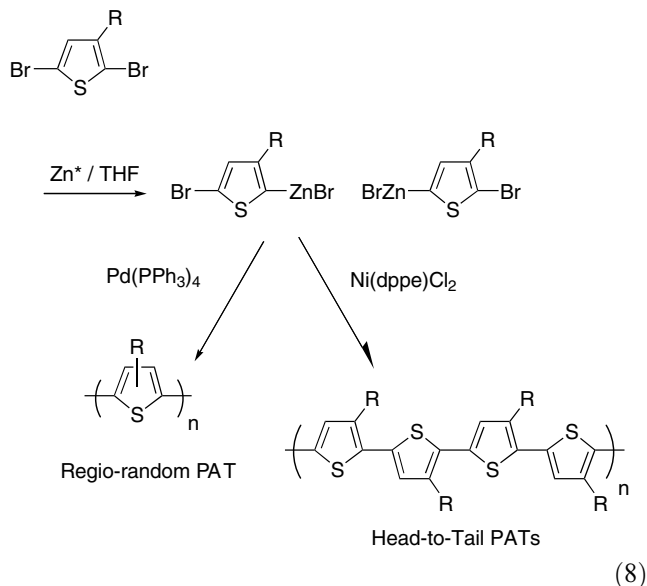
The side chain can contain electrochemically active group (e.g. **1**) [20]. The mercapto-substituted side chain (e.g. **2**) synthesized by the same method can be used in soft-lithography patterning [21].



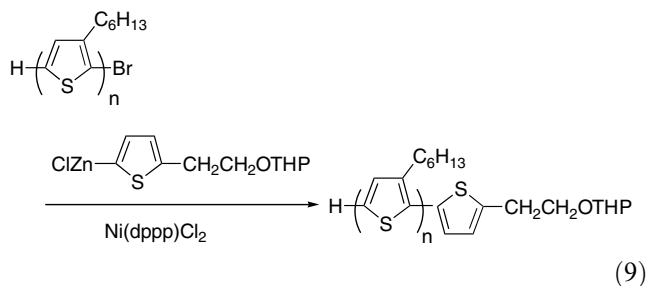
Starting from 2-bromo-3-[2-(*S*-methylbutoxy)ethyl]-thiophene, the corresponding polymer is synthesized using McCullough method (Eq. (6)) [22]. At 160 °C, the melting point of the polymer, a complete loss of optical activity in the  $\pi$ - $\pi^*$  transition band is observed. Slow cooling of the polymer film yields a reversible thermochromism, while the optical activity in the absorption bands is recovered. The MgBr moiety can also be obtained by the metathesis with a Grignard reagent (Eq. (7)) [23].



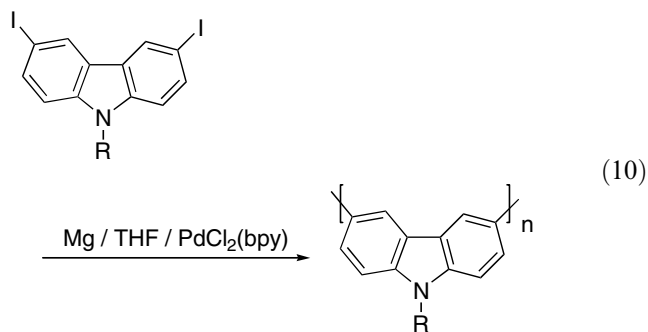
Highly reactive zinc [24] reacts chemoselectively with 2,5-dibromothiophene to yield quantitatively 2-bromozincio-5-bromothiophene. In the presence of Pd(PPh<sub>3</sub>)<sub>4</sub>, poly(thiophen-2,5-diyl) is obtained [25]. However, under the same conditions, 3-hexyl analog yields regio-random structure in the product polymer. When NiCl<sub>2</sub>(dpe) is employed, 90% regioselectivity, however, is observed (Eq. (8)) [25].



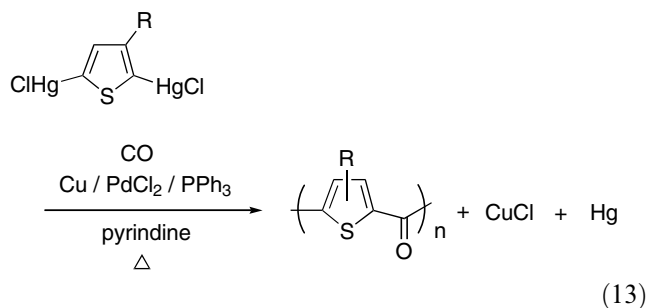
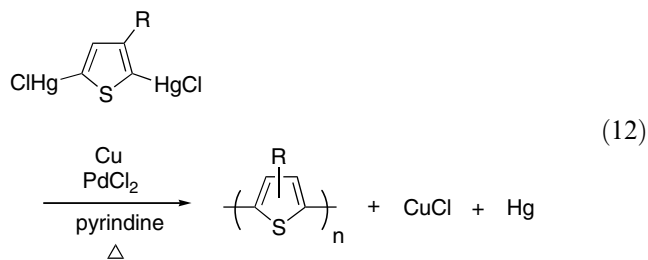
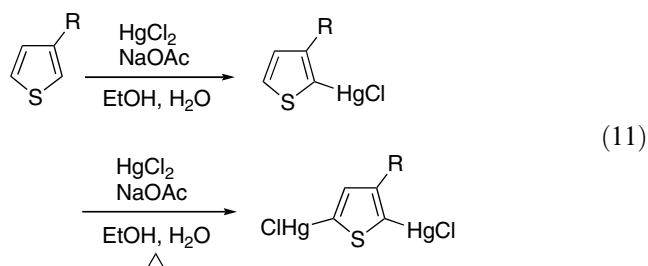
The end group modification of regio-regular polythiophenes can be achieved by the nickel-catalyzed cross-coupling reaction of 2-thienylzinc reagent (Eq. (9)) [26].



The reaction can also be extended to the synthesis of poly(9-alkylcarbazole-3,6-diyl)s via palladium-catalyzed cross-coupling reactions (Eq. (10)) [27].



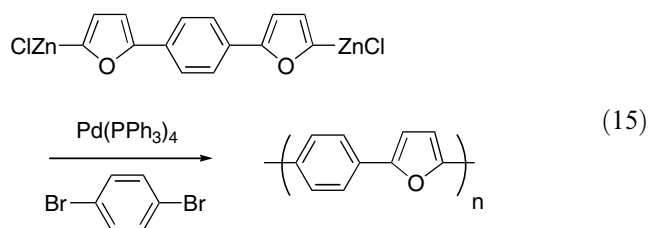
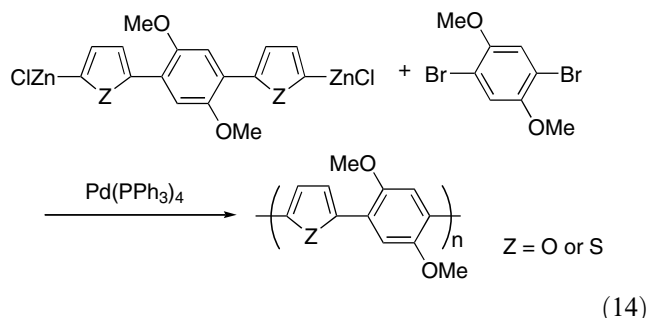
Palladium-catalyzed reductive coupling of thienyl mercuric chloride (Eq. (11)) yields the corresponding poly(3-alkylthiophene)s (Eq. (12)) [28]. In the presence of a CO atmosphere, alternating poly(thiophenediyl ketone)s are obtained in moderate yield (Eq. (13)). Copolymerization of two different dimeric chlorides afford the corresponding copolymers.



The use of furan-containing conjugated systems in material application has been rare because the heteroaromatic ring may be susceptible to photoinduced oxida-

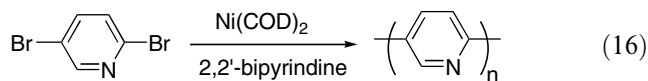
tive cleavage [29]. However, it has recently been shown that furan moiety is stable under inert atmosphere upon irradiation even at elevated temperature [30].

Reactions of bis-zinc chloride and dibromobenzene derivatives in the presence of a catalytic amount of  $\text{Pd}(\text{PPh}_3)_4$  lead to the formation and precipitation of the corresponding polymers (Eqs. (14) and (15)) [31]. The corresponding thiophene analog is prepared similarly. Electrical conductivities are enhanced when these polymers are doped with  $\text{I}_2$  or  $\text{FeCl}_3$ .

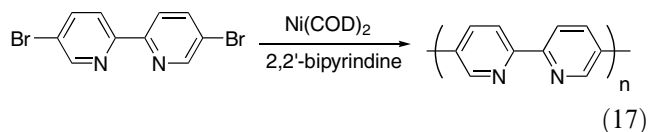


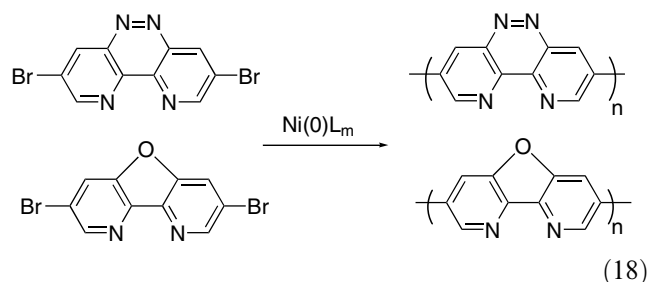
### 3. Yamamoto coupling

Ni(0)-based polymerization of 2,5-dibromopyridine yields the corresponding poly(2,5-pyridinediyl) as yellow or yellowish orange precipitate (Eq. (16)) [32–34].

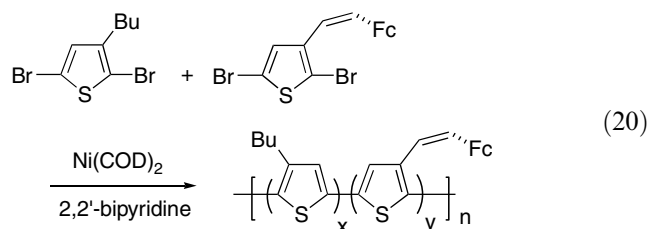
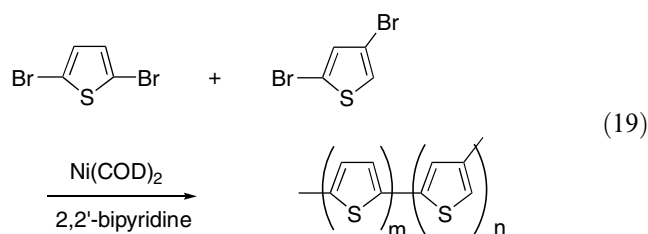


It is interesting to note that the presence of 1 mole  $\text{Ph}_3\text{P}$  per mole of Ni gave higher yield and higher molecular weight than those in the reaction system containing excess amount of  $\text{Ph}_3\text{P}$ . In this case, both head-to-tail and tail-to-tail units are present. In order to avoid such irregularity, polymerizations of bipyridine derivatives lead to regio-regular polybipyridines (Eqs. (17) and (18)) [35].



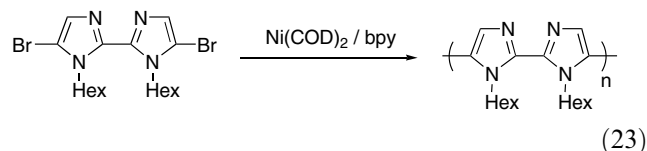
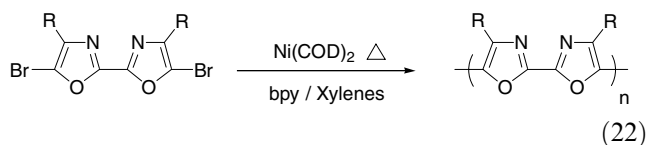
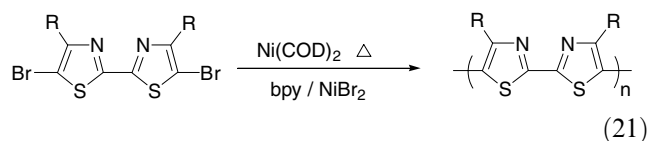


The corresponding monomers are also synthesized by means of cross-coupling reactions. The reaction has been extended to the synthesis of poly(thiophene-2,5-diyl)s [36]. Copolymers derived from 2,5-dibromothiophene and 2,4-dibromothiophene are also synthesized by this procedure (Eq. (19)) [36]. Ferrocene bearing polythiophene copolymers are prepared similarly (Eq. (20)) [37].

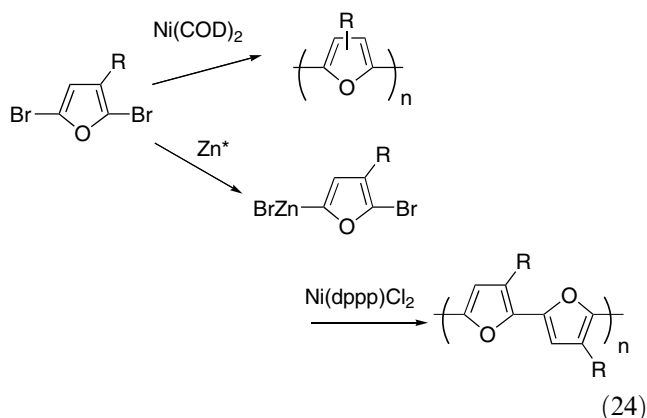


Dehalogenative couplings of 4,4'-dialkyl-2,2'-bithiazoles with Ni(0) in refluxing toluene yield the corresponding new class of variable bandgap conjugated polymers having thermochromic properties (Eq. (21)) [38]. These polymers are capable of reversible n-doping with a maximum doping level of about one electron per bithiazole unit. This capacity is comparable to that of  $(\text{Li}_{0.1}\text{CH})_x$  and greater than the usual capacities of common *p*-dopable conjugated polymers.

The corresponding oxygen analog, poly(nonylbisoxazole) (Eq. (22)) [39] and nitrogen analog, poly(imidazole-2,5-diyl)s (Eq. (23)) [40] are prepared similarly. These polymers are electrochemically active and have stacked structures in the solid.

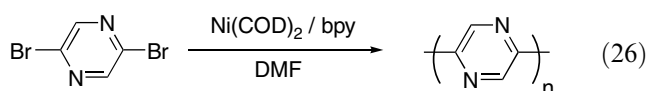
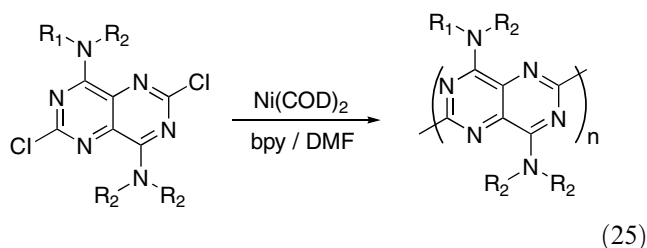


Polymerization of 3-alkyl-2,5-dibromofuran has been studied in details (Eq. (24)) [41]. When Ni(COD)<sub>2</sub> is used, 75% of head-to-tail regio-regularity is obtained. Zinc procedure by Rieke method followed by treatment with a catalytic amount of NiCl<sub>2</sub>(dpep) yield over 95% regioselectivity favoring head-to-tail linkage.

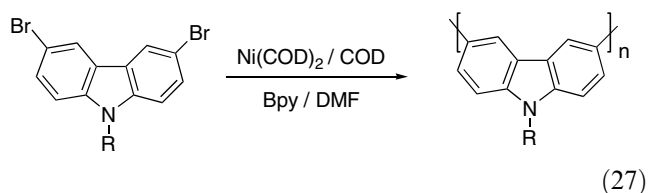


On the other hand, the same organozinc intermediate is transformed into random linkage when Pd(PPh<sub>3</sub>)<sub>4</sub> is employed as the catalyst. The physical as well as spectroscopic properties of these polymers are very much dependent on the regio-regularity.

New n-type poly(pyrimido[5,4-d]pyrimidine-2,6-diyl)s are prepared from the Ni(0) promoted coupling reaction of the corresponding monomeric chlorides in excellent yields (Eq. (25)) [42]. Poly(pyrazine-2,5-diyl) is prepared in a similar manner (Eq. (26)) [43].



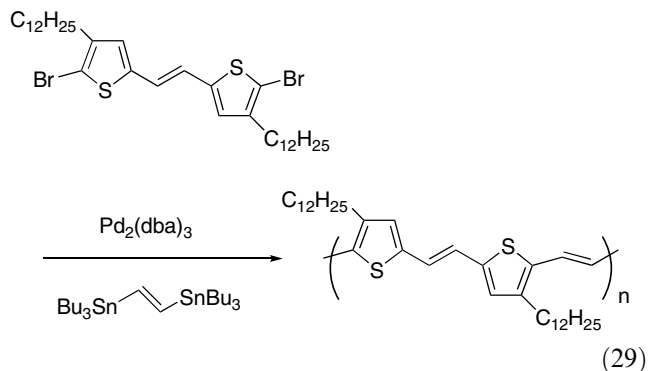
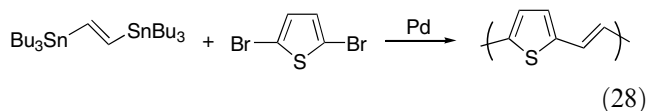
Polymerization of *N*-alkyl-3,6-dibromocarbazoles under Yamamoto coupling conditions yields the corresponding high molecular weight polycarbazoles with good solubility, film-forming ability, thermal stability and moderately high photoluminescence efficiency (Eq. (27)) [44].



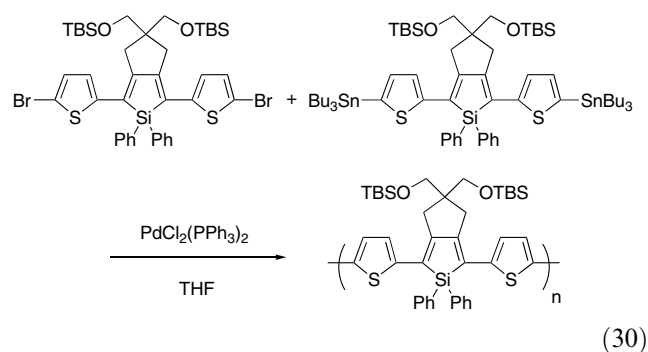
#### 4. Stille coupling

The cross-coupling reaction of dihalogenothiophene compounds and 1,2-bis(tributyl)stannylethene catalyzed by palladium phosphine complexes, known as Stille coupling reaction [45], is found to provide a new simple route to conducting poly(thiophene-2,5-diyl-vinylene) (Eq. (28)) [46].

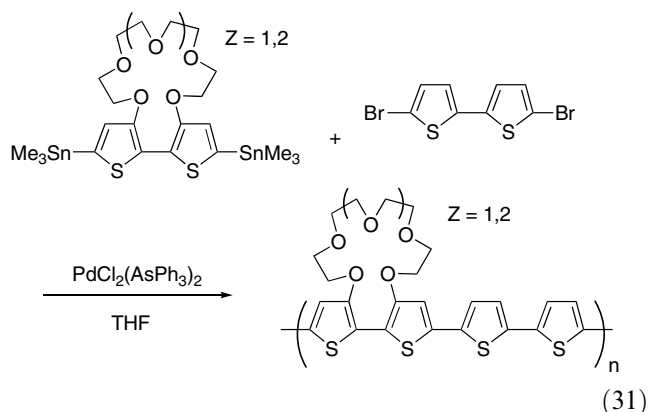
Regio-regularity can be controlled by using 5,5'-dibromo-2,2'-dithienylethene as the starting material (Eq. (29)) [47].



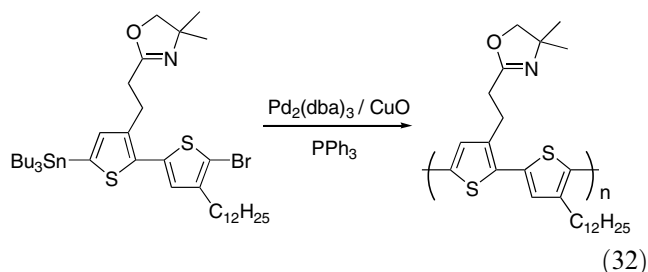
The reaction has been extended to the synthesis of thiophene-silole copolymer (Eq. (30)) [48] which shows broad absorptions at 594 and 615 nm. This unusual long wavelength absorption suggests the occurrence of intramolecular charge transfer from thiophene ring to silole ring.



Substituted polythiophenes are an ideal choice for a sensory material due to their ease of structural modification, high conductivity, and environmental stability [49,50]. The conductivity of these materials is sensitive to the nature and regiospecificity of the side chains, indicating that small change of conformation may produce large effects [49,51]. Crown ether-containing polythiophenes are obtained from the Stille coupling reaction of a distannane with a dibromide (Eq. (31)) [52]. Ionochromic response has been found in these polymers in the solution state.

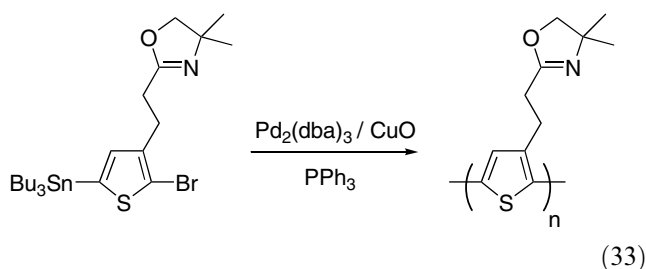


Amphiphilic and regio-regular polythiophenes are obtained by Stille coupling of the dithiophene containing bromide and stannyl group at 5 and 5' positions (Eq. (32)) [53].

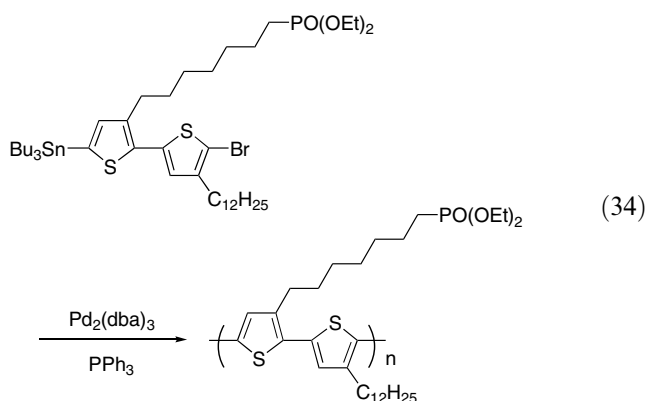


Regio-regular oxazoline polythiophene is obtained from the reaction of the corresponding monomer in high yields by using a CuO-modified Stille coupling route

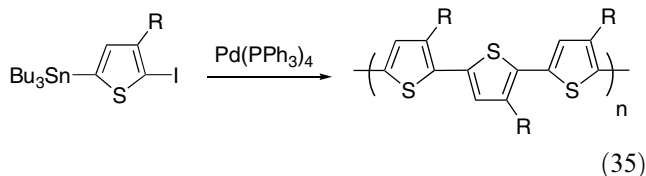
(Eq. (33)) [54]. The oxazoline moiety can be hydrolyzed into the carboxylic acid group. Under basic conditions, the polymer shows the cation size-dependent chromaticity.



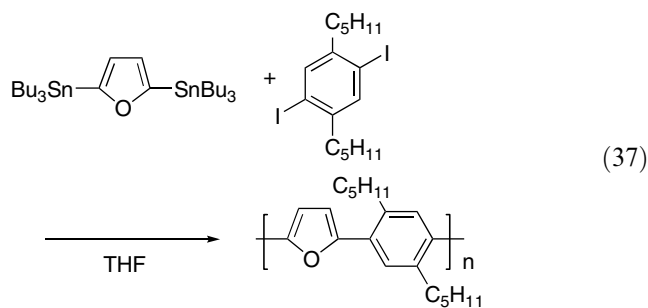
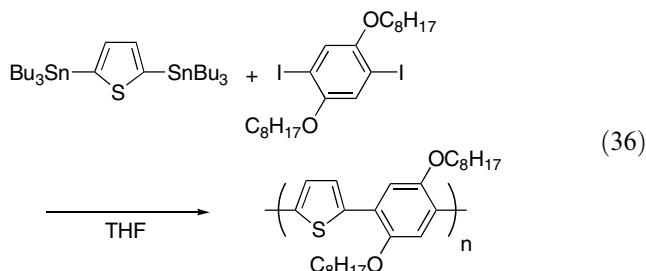
The phosphonic acid functionalized polythiophenes are prepared similarly (Eq. (34)) [55].



On increasing the ratio of head-to-tail coupling of adjacent monomers on poly(3-alkylthiophenes), an increase in linearity of polymer chains and hence greater conjugation along the polymer backbone and lower band gap are observed. Thus 2-iodo-3-hexyl-5-stannylthiophene is treated under Stille coupling reaction to yield highly regio-regular poly(3-hexylthiophene) with head-to-tail coupling ratios exceeding 96% (Eq. (35)) [56].

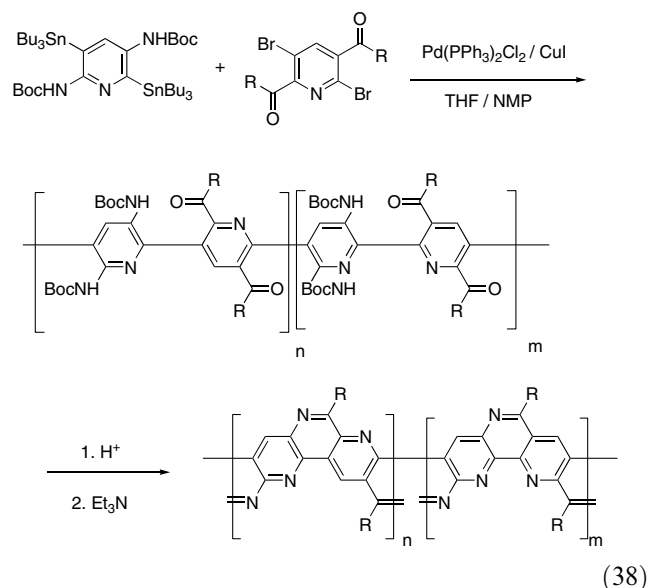


Alternating thiophene-dialkoxyphenylene [57] and phenylene-furan [29b] copolymers are synthesized similarly (Eqs. 36 and 37).



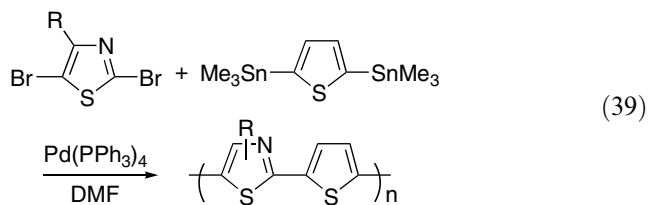
The Stille coupling reaction is used to synthesize photorefractive polymer that contains a conjugated backbone and a second order non-linear optical chromophore [58]. It is interesting to note that a combination of an electron-rich distannyl monomer and an electron deficient dihalide monomer forms polymers with relatively high molecular weights [59]. In addition, solvents, that could keep the macromolecules in solution and stabilize the palladium catalyst, would yield polymers with high molecular weights.

Pd/Cu-catalyzed couplings of dibromopyridines with distannylpyridines are utilized for the synthesis of functionalized polypyridines for double-bonded ladder polymers (Eq. (38)) [60].



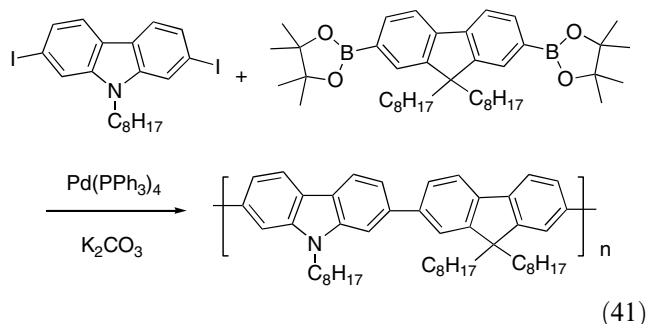
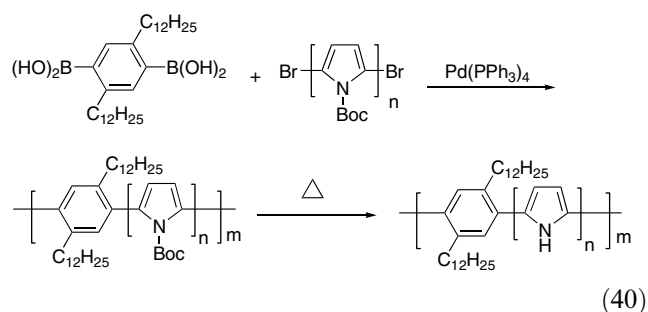
Palladium-catalyzed polycondensation between 2,5-dibromo-4-alkylthiazoles and 2,5-(bistrimethylstannyl)thiophene gives charge-transferred-type alternating polymers of high regio-regularity (Eq. (39)) [61]. The tendency of the polymer to form the stacked structure is considered to contribute to the regio-regulation in the polymerization.



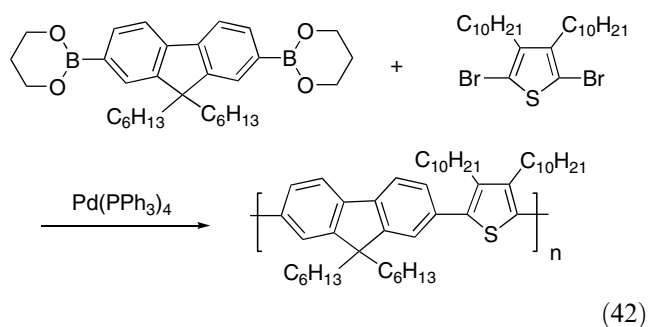


### 5. Suzuki–Miyaura coupling

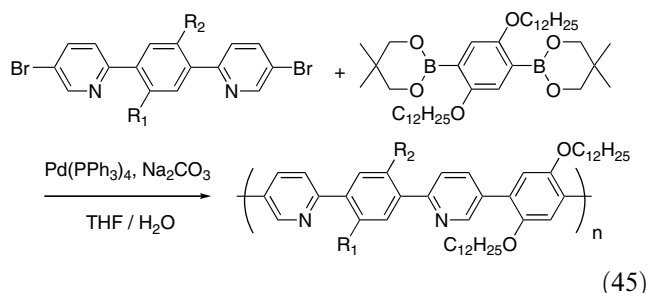
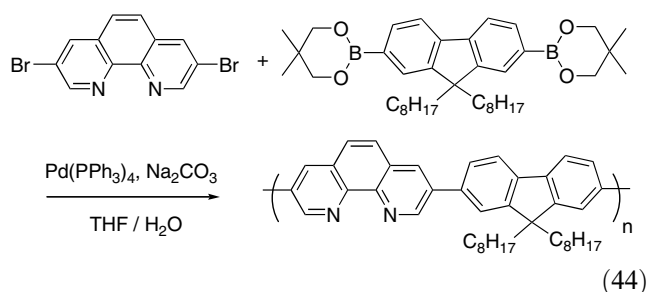
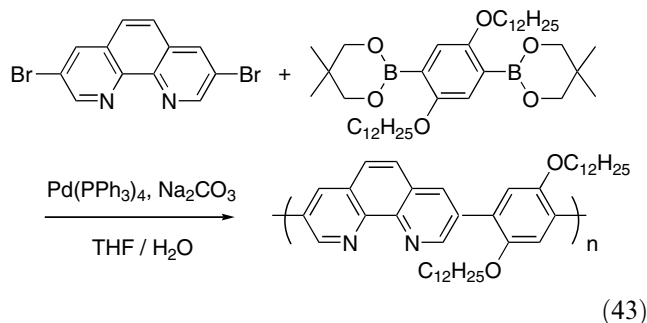
Suzuki–Miyaura reaction is also a powerful tool for the formation of  $\text{C}_{\text{sp}2}\text{--}\text{C}_{\text{sp}2}$  bond [62]. Thus, polymers containing alternating phenylene and pyrrolic or terpyrrolic units are prepared by the Suzuki–Miyaura coupling reaction of the corresponding bisboronic acid and bis halides (Eq. (40)) [63]. In a similar manner, poly(carbazole-2,7-diylfluorene-2,7-diyl) is prepared from the corresponding monomers (Eq. (41)) [64].



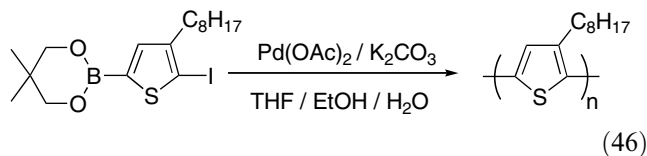
Blue-light emitting fluorene-based polymers with tunable electronic properties are obtained from Suzuki–Miyaura coupling reaction (Eq. (42)) [65].



Thermally stable polymers comprised of alternating 1,10-phenanthroline/1,4-didodecyloxybenzene, 1,10-phenanthroline/9,9-dioctylfluorene or pyridine/1,4-dialkoxybenzene units are synthesized by palladium(0)-catalyzed coupling reaction in excellent yields (Eqs. (43)–(45)) [66].

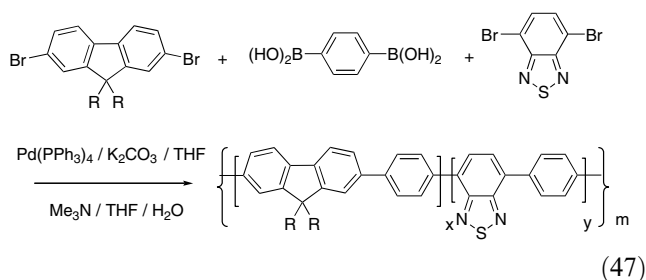


Like Stille coupling reaction, the Suzuki–Miyaura reaction can also be highly regio-regular (96% head-to-tail), when 3-alkylthiophene derivatives are employed (Eq. (46)) [67].

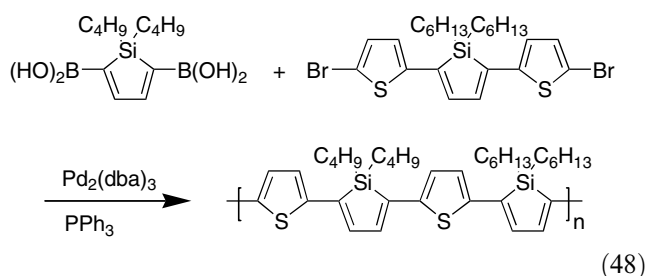


Suzuki–Miyaura copolymerization of *p*-phenylenebisboronic acid with a mixture of 4,7-dibromo-2,1,3-benzothiadiazole and a 2,7-dibromofluorene derivative affords the corresponding copolymer which is then transformed into polycationic water soluble conjugated copolymer that changes emission color as a result of conformational and aggregation changes (Eq. (47)) [68].



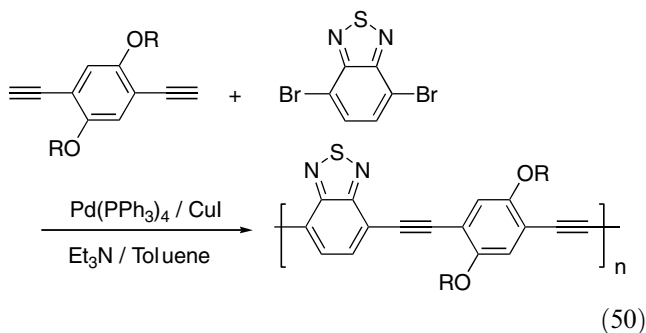
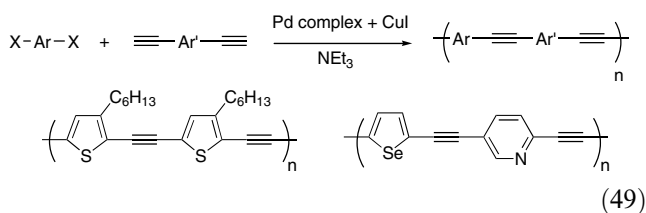


The synthesis of alternating silole-thiophene copolymer is achieved by the Suzuki–Miyaura coupling reaction (Eq. (48)) [69]. Silole–phenylene, silole–pyridine and silole–thiazole alternating copolymers are prepared similarly [70].

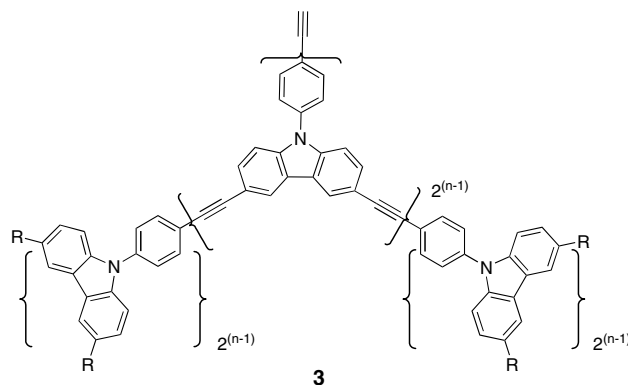


## 6. Sonogashira coupling

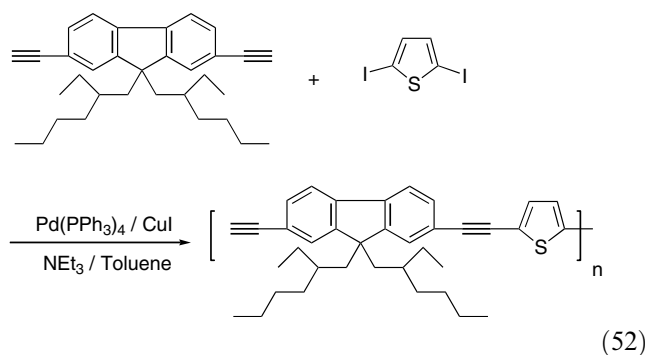
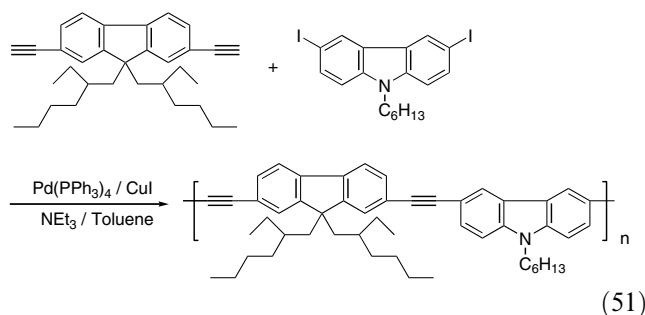
Sonogashira reaction [71] provides a useful route leading to the formation of  $C_{sp}-C_{sp2}$  bond. Thus, palladium-catalyzed polycondensation between dihaloheteroaromatic compounds and ethynyl aromatic compounds in the presence triethylamine gives soluble  $\pi$ -conjugated polyaryleneethynylene type polymers (Eqs. (49) and (50)) [72].



9-Phenylcarbazole ethynylene monodendrons (e.g. **3**) with 1,1, 3,3,-tetramethylbutyl and 3,5-di-*tert*-butyl-4-(2-methoxyethoxy)phenylene groups are used for the synthesis up to generation four of dendrimers [73].



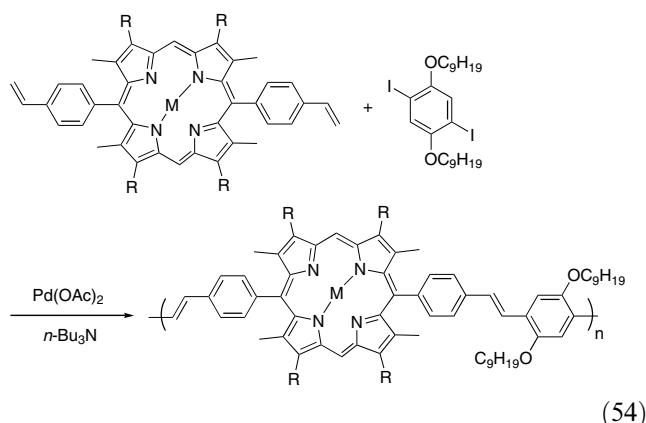
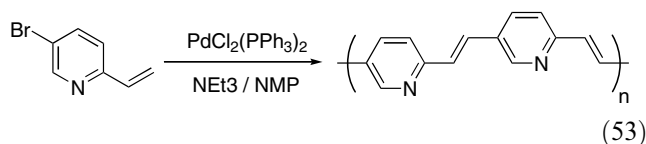
A series of light-emitting poly(aryleneethynylene) based on fluorenes with sterically hindered substituents containing hole transport unit such as carbazole and thiophene are synthesized by a palladium-catalyzed coupling reaction (Eqs. (51) and (52)) [74].



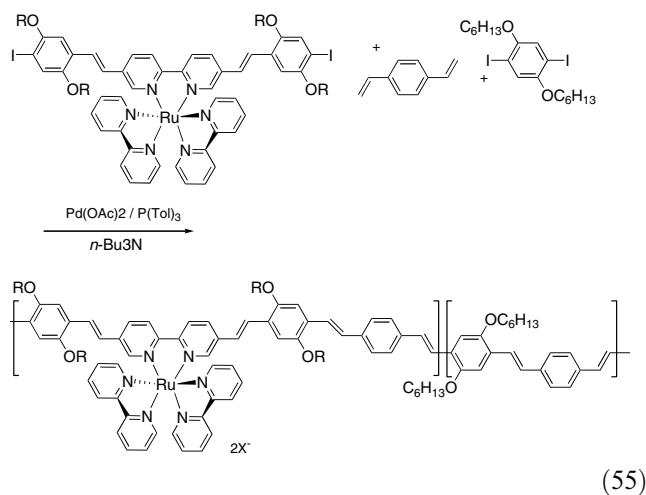
## 7. Heck reaction

Poly(phenylene vinylene) (PPV) and its derivatives have received much attention due to their high conductivity and optoelectronic properties for electroluminescent applications [75]. The Heck reaction has been successfully applied to synthesize several PPVs [76]. It has been shown that electron deficient PPV analogs may exhibit highly efficient

light emitting diodes [77]. It is therefore envisaged that the corresponding pyridinium ion analogs, poly(methylpyridinium-vinylene)s (PMPyV), may demonstrate a similar effect [76]. The charged polymers PMPyV can be readily obtained from methylation of the corresponding poly(*p*-pyridyl vinylene)s (PPyVs). The head-to-tail regioisomer is synthesized by the Heck reaction (Eq. (53)) [78]. Metalloporphyrin containing polymers can also be obtained by a similar reaction (Eq. (54)) [79].

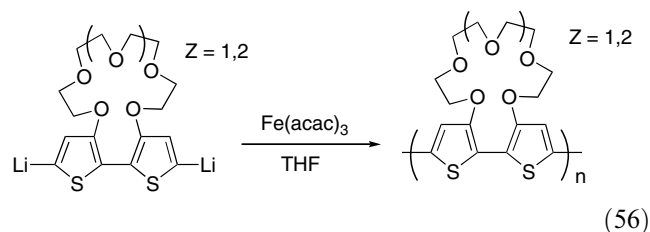


Photoconductive ruthenium-containing conjugated copolymers are prepared from the palladium-catalyzed Heck coupling reaction (Eq. (55)) [80]

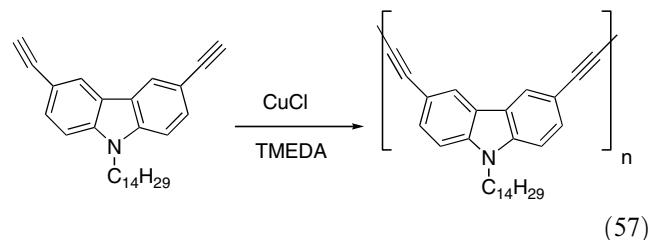


## 8. Miscellaneous reactions

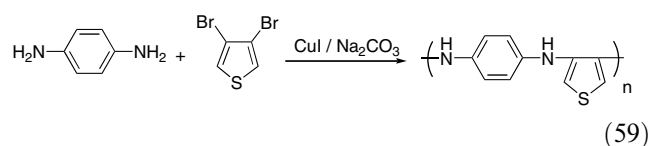
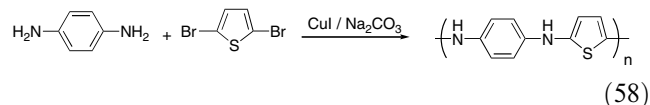
Fe(acac)<sub>3</sub>-promoted oxidative polymerizations of crown ether-containing dilithium-dithiophene yield the corresponding polymers which can selectively bind to alkali metal ions (Eq. (56)) [52].



Poly(3,6-dibutadiynyl-9-tetradecylcarbazole), which can serve as hole transporting materials, is synthesized by the CuCl induced polymerization (Eq. (57)) [81].



The condensation of 2,5-dibromothiophene or 3,4-dibromothiophene with 1,4-diaminophenylenes under Ullmann conditions in the presence of cuprous iodide and sodium carbonate yields a series of aniline-thiophene copolymers (Eqs. (58) and (59)) [82].



## 9. Conclusion

We have summarized the recent advances on the use of cross-coupling reactions for the preparation  $\pi$ -conjugated heteroaromatic polymers for optoelectronic interests. Polymers of different fascinating structural variety can be easily accessed by this methodology. As the development of optoelectronic materials grows so rapidly in recent years, the applications of organometallic chemistry for the preparation of these polymeric materials will continuously be flourishing in the years ahead.

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