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Electron Donor-Acceptor Organic Polymers by "Click" Type Cycloaddition/ Retroelectrocyclization Reaction

Wenyi Huang

Abstract

The "click" type cycloaddition/retroelectrocyclization reaction is an intriguing approach for synthesizing electron donor-acceptor organic polymers. This chapter covers the fundamental reaction mechanism and the basic principles of applying this reaction to the synthesis of organic polymers via postfunctionalization or step-growth polymerization. The electron donor-acceptor moieties can be incorporated into the main-chain and/or side-chain of both conjugated and nonconjugated polymers. These polymers feature attractive properties including intramolecular charge-transfer bands, nonlinear optical properties, redox activities, third-order nonlinear optical properties, and enhanced thermal stability. Because of this, these polymers have found a variety of applications such as colorimetric chemosensors of metal ions, nonlinear optics, and solar cells. This novel "click" chemistry paves a unique path toward the synthesis of next-generation functional materials that cannot be accomplished by the incumbent synthetic methods.

Keywords: electronic donor-acceptor polymers, click reaction, cycloaddition/retroelectrocyclization reaction

1. Introduction

The "click" chemistries such as Diels-Alder cycloaddition, Cu-catalyzed azide/ alkyne cycloaddition (CuAAC), and thiol-ene reaction have revolutionized the polymer science over the past two decades and have become an indispensable tool in synthesizing new polymers or incorporating new functionality into macromolecules [1–10]. In recent years, a new "click" chemistry of cycloaddition/retroelectrocyclization reaction has gained momentum in both organic synthesis and polymer synthesis. The "click" type cycloaddition/retroelectrocyclization reaction was first discovered by Bruce et al. [11] for the synthesis of metal acetylides in the 1980s. The first step of cycloaddition/retroelectrocyclization reaction involves the reaction of electron-rich alkynes activated by strong electron-donating groups (EDGs) with a strong electron-accepting cyanoolefinic molecule via a [2+2] cycloaddition to form the cyclobutene rings, and in the subsequent step, these cyclobutene rings are spontaneously opened to produce the donor-acceptor type chromophores in quantitative yields under mild conditions [12]. The currently available electron-donating groups for almost quantitative yields include aromatic amines [13–16], ferrocene [17, 18],

azulene, and organometallic derivatives [19, 20]. Examples of electron-accepting cyanoolefinic molecules are tetracyanoethylene (TCNE), 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its derivatives [21–24], as well as dicyanovinyl and tricyanovinyl derivatives [25, 26]. Among these electron-accepting molecules, TCNE is one of the strongest organic electron acceptors, and its high chemical reactivity toward nucleophiles or electron-rich reagents is frequently used to introduce strong acceptor moieties, for example, 1,1,4,4-tetracyanobuta-1,3-diene (TCBD), into organic molecules [27, 28]. The cycloaddition/retroelectrocyclization reaction mechanism between TCNE and electron-rich alkynes activated by an electron-donating group (EDG) is illustrated in **Figure 1**. By leveraging the same chemistry, TCNQ can also react with electron-donating group substituted alkynes to exclusively yield the thermodynamically stable Z-isomer, as demonstrated in **Figure 2** [29].

Over the past decade, this "click" chemistry of cycloaddition/retroelectrocyclization reaction has been extensively used to synthesize electron donor-acceptor type organic molecules or dendrimers, which exhibit many interesting electrical, electrochemical, or nonlinear optical properties [30–33]. Very recently, this synthetic protocol has been generalized into macromolecular systems through step-growth polymerization or postfunctionalization due to the high reactivity of this reaction [12]. In particular, most of these polymers were realized by the postfunctionalization reaction of precursor polymers containing activated alkynes with TCNE or TCNQ. These electron donor-acceptor polymers can be classified into two major categories, namely, main chain and side chain, depending on the location of electron donor-acceptor chromophores in the macromolecular chain. For main-chain electron donor-acceptor conjugated polymers, the precursor polyyne polymers often contain electron-donating moieties such as ferrocene [34], carbazole [35], thiophene [36], and metal acetylide [37]. However, only partial adduction of TCNE or TCNQ occurred, which was attributed to the low electron-donating property of electron donors as well as the high steric hindrance in the main chain [38]. To address this challenge, Huang [38] synthesized a poly(arylene ethynylene)
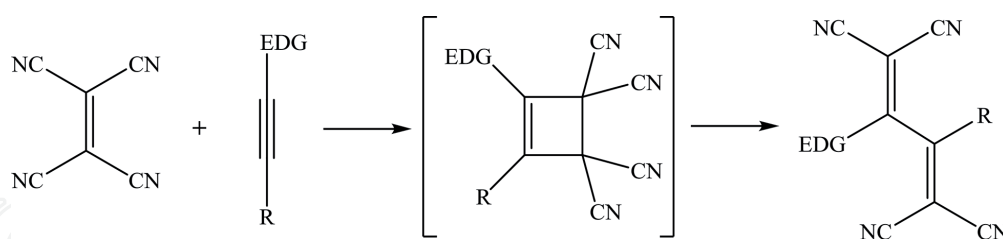
Figure 1.
Cycloaddition/retroelectrocyclization reaction mechanism between tetracyanoethylene and electron-rich alkynes activated by an electron-donating group (EDG).
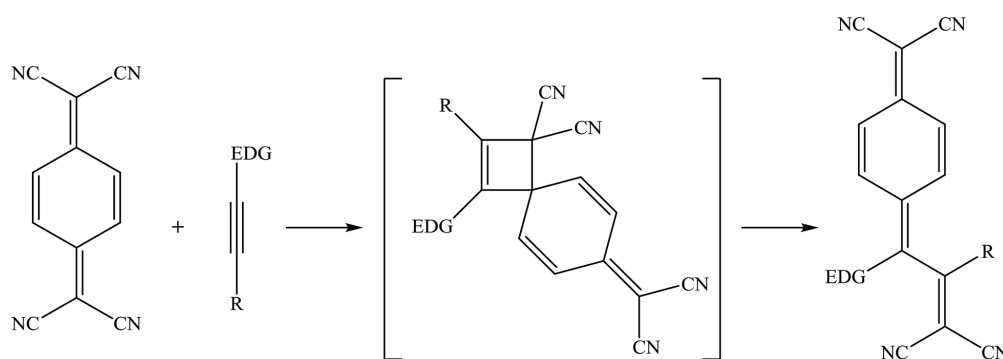
Figure 2.
Cycloaddition/retroelectrocyclization reaction mechanism between 7,7,8,8-tetracyanoquinodimethane and electron-rich alkynes activated by an electron-donating group (EDG).

having dialkylanilino groups in the para-position relative to the ethynyl groups, which possess the strongest electron-donating effect on alkynes and thus enable the complete reaction of all alkynes in the main chain with TCNE to afford alternating electron donor-acceptor main-chain polymers. On the other hand, main-chain donor-acceptor nonconjugated polymers often involve a TCNQ-containing molecule and an aniline-activated alkyne molecule by cycloaddition/retroelectrocyclization reaction [39]. Furthermore, side-chain electron donor-acceptor polymers were generally synthesized from precursor polymers bearing dialkylaniline-substituted alkyne side chains [40, 41]. In contrast to main-chain alkynes, side-chain alkynes showed reactivity as high as the corresponding small molecules, probably due to the lowered steric hindrance [40]. Thus, the full TCNE (or TCNQ) addition to the polymer side chains could be achieved.

One of the striking features of cycloaddition/retroelectrocyclization reaction is that it does not involve any metal catalysts, and this reaction typically proceeds rapidly under mild conditions with very good yields [28]. Furthermore, the resulting molecular structure shows not only tunable redox activities in both the cathodic and anodic directions but also strong charge-transfer bands in the visible absorption region [39]. The TCNQ adducts exhibited a more bathochromically shifted absorption (usually a green color) as compared to the counter TCNE adducts (usually a red color) because of the extended π-conjugation [39, 42, 43]. The characteristics of click chemistry meet all the prerequisites required by the polymer synthesis. A very high yield of cycloaddition/retroelectrocyclization reaction is one of the essential parameters to obtain high-molecular-weight polymers by the step-growth polymerization [42]. In addition, a lack of side products for cycloaddition/retroelectrocyclization reaction is desirable. Generally, the synthesis of small molecules can be purified by distillation or chromatography techniques. Unfortunately, it is rather difficult to separate undesired subunits from polymers caused by side reactions. These donor-acceptor polymers display an enhanced thermal stability compared with the precursor polymer, which was attributed to the reinforced intermolecular interactions caused by the cyano groups [38].

The low bandgap energy of π-conjugated polymers is vital for their applications in many emerging areas such as organic photovoltaic devices, light-emitting diodes, and nonlinear optical devices [41]. The bandgap energy (Eg) of π-conjugated polymers may be defined by $E_g = E_{LUMO} - E_{HOMO}$ [44, 45], in which E_{HOMO} is the highest occupied molecular orbital (HOMO) energy and E_{LUMO} is the lowest unoccupied molecular orbital (LUMO) energy. E_g can be effectively reduced by enhancing the strength of electron donors and/or acceptors through the intramolecular charge-transfer interactions. As a result, the E_{HOMO} level of the donor and the E_{LUMO} level of the acceptor are closer than those in pristine systems, leading to narrower Eg [41]. In order to achieve a lower Eg of conjugated polymers, the strength of both electron-donating and electron-accepting units must be further improved, which can be accomplished by employing stronger electron-donating groups like dialkylamine on the donor to raise the E_{HOMO} as well as stronger electron-withdrawing groups such as –CN group on the acceptor to reduce the E_{LUMO} [44, 45].

Furthermore, another important application of electron donor-acceptor polymers synthesized by cycloaddition/retroelectrocyclization reaction is for the use as colorimetric ion sensors, although their detection limits are usually inferior to those of fluorescent ion sensors. The nonplanar donor-acceptor chromophores in these polymers displayed the selective recognition of certain ions such as Fe^{3+}, Fe^{2+}, Sn^{2+}, and Ag^+ ions for the TCNE adducts and Fe^{3+}, Cu^{2+}, Ti^{4+}, Sc^{3+}, and Ag^+ ions for the TCNQ adducts [46, 47]. The recognition usually occurs at the aniline nitrogen, resulting in a decrease in the charge-transfer bands accompanied by visual color changes.

This chapter aims to provide an overview of the state-of-the-art development of electron donor-acceptor organic polymers synthesized by the "click" type cycloaddition/retroelectrocyclization reaction, thereby elaborating on the synthetic approaches for both main-chain and side-chain polymers as well as their applications.

## 2. Synthesis of electron donor-acceptor organic polymers

Over the past decade, a wide variety of functional polymers have been synthesized by cycloaddition/retroelectrocyclization reaction [48]. Among the synthetic protocols, postfunctionalization of precursor polymers bearing electron-rich alkynes with a strong electron acceptor is the most extensively employed technique for preparing electron donor-acceptor polymers because of the high reactivity and high yield of cycloaddition/retroelectrocyclization reaction [12].

### 2.1 Main-chain electron donor-acceptor organic polymers

2.1.1 Main-chain electron donor-acceptor conjugated polymers

Low bandgaps of conjugated polymers are highly preferred for many important applications such as solar cells, light-emitting diodes, field-effect transistors, and supercapacitors [49–53]. The bandgap energy of conjugated polymers can be effectively reduced by introducing electron donor-acceptor chromophores into these polymers, primarily arising from the intramolecular charge-transfer interactions between electron donor and acceptor [44, 45]. TCNE and TCNQ are among the strongest electron acceptors [54], but they are sparsely employed for synthesizing donor-acceptor type conjugated polymers. The underlying reason lies in the difficulty in synthesizing TCNE or TCNQ derivatives that are suitable for polymerization. In addition, many conventional approaches for synthesizing conjugated polymers, especially those involved with the use of metal ion catalysts (e.g., palladium or nickel), are not appropriate for the use in synthesizing polymers having TCNE or TCNQ derivatives, because these TCNE or TCNQ derivatives would always form strong complexes with these metal ion catalysts leading to the reduction in their catalytic performance [55]. As a result, electron donor-acceptor conjugated polymers involving TCNE and TCNQ must be done by the postfunctionalization approach.

The postfunctionalization approach was first explored by Michinobu for ferrocene-containing poly(aryleneethynylene)s [34]. Slow heating to 120°C for 3 h was required to facilitate the cycloaddition/retroelectrocyclization reaction between ferrocene-containing poly(aryleneethynylene)s and TCNE, and the completion of reaction was evidenced by the color change of the reaction solution from orange to green. However, only partial adduction of TCNE occurred, for example, the TCNE addition amounted to 0.75 and 0.62 for **P1** and **P2**, respectively. This was attributed to the decreased electron-donating power of the ferrocene donor substituted by the TCBD acceptor as well as the high steric hindrance in the main chain. The excess of TCNE did not cause any undesired side reactions and was removed by sublimation or reprecipitation. Both **P1** and **P2** featured well-defined intramolecular charge-transfer absorption bands and redox activities in both anodic and cathodic directions.
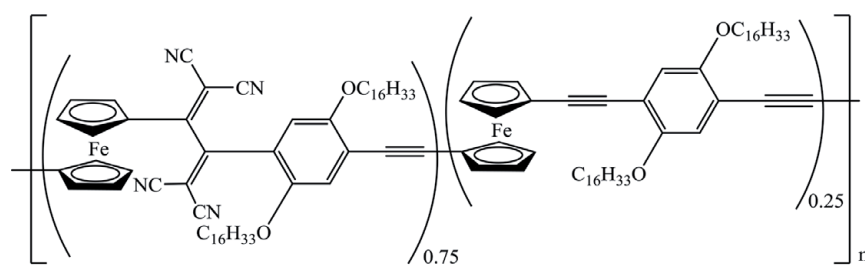
P1
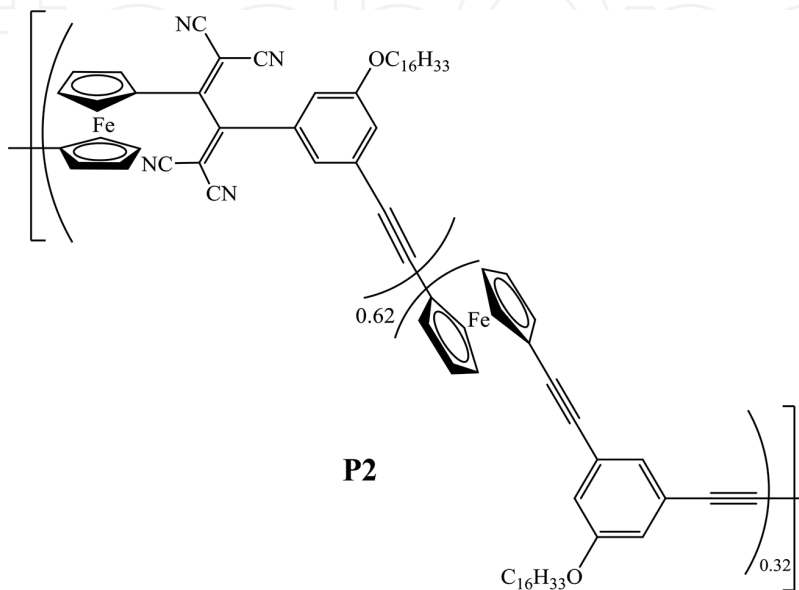
P2

Furthermore, carbazole was selected as an electron-donating group, and the corresponding poly(arylenebutadiynylene)s were prepared by the acetylenic oxidative polymerization [56]. The substitution pattern of carbazole had a significant influence in the efficiency of the cycloaddition/retroelectrocyclization reaction. For example, 3,6-carbazole-based poly(arylenebutadiynylene) was successfully converted into the donor-acceptor type conjugated polymer, whereas the 2,7-carbazole-based counterpart polymer did not react with TCNE due to the insufficient activation of alkyne moieties. Upon the optimization of reaction conditions, 0.75–0.8 equiv. of TCNE was successfully reacted with main-chain alkynes of 3,6-carbazole-based poly(arylenebutadiynylene), resulting in the donor-acceptor conjugated polymer, **P3**. This conjugated polymer showed strong intramolecular charge-transfer interactions as well as higher thermal stability having a thermal degradation temperature above 350°C.
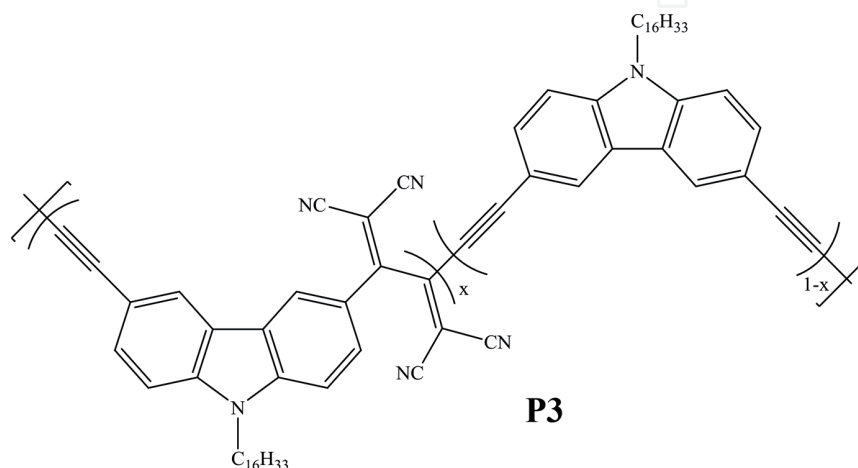

P3

Thiophene is another important electron-donating moiety, and it has been incorporated into poly(thienyleneethynylene) by the Sonogashira polycondensation of 2-bromo-5-ethynyl-3-hexylthiophene [36, 56]. TCNE and TCNQ were employed to react with poly(thienyleneethynylene) in the presence of microwave irradiation to afford **P4** and **P5**, respectively. These two donor-acceptor conjugated polymers displayed an enhanced thermal stability as compared with the precursor polymer, arising from the reinforced intermolecular interactions caused by the cyano groups. UV-Vis-NIR spectroscopy revealed charge-transfer bands in the low-energy region, while electrochemistry confirmed the narrower bandgaps with the elevated HOMO and lower LUMO levels relative to the precursor polymer. After doping, these polymers showed room temperature conductivities of as high as 4.5×10^{-5} S/cm, which was about ten times greater than that of the precursor polymer.

P4

P5
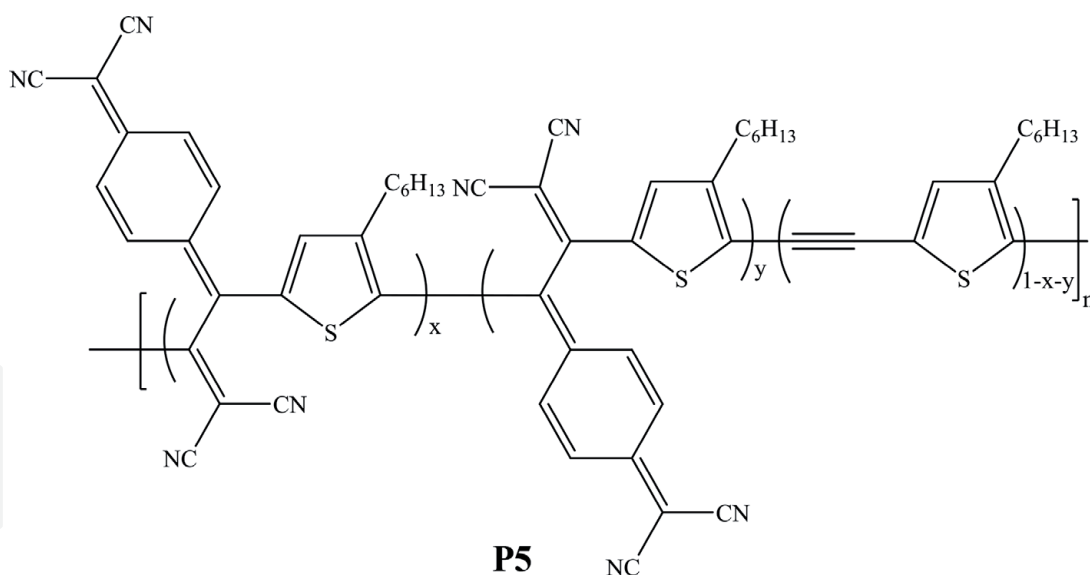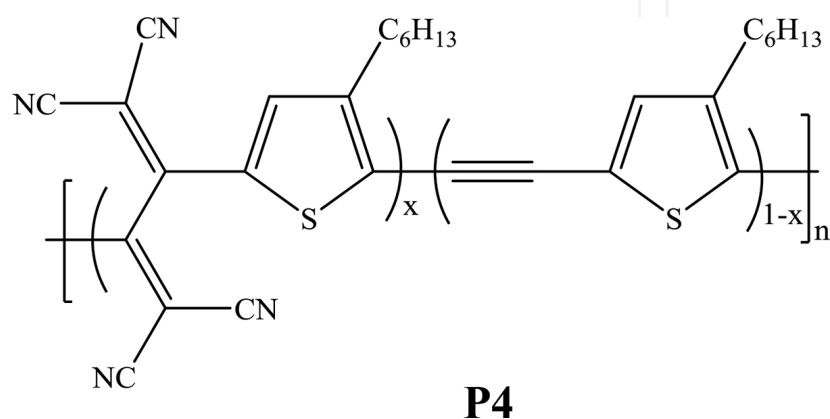
Ohshita et al. [57] reported the reaction of poly(disilanyleneethynyleneoligoth ienyleneethynylene)s with TCNE to yield new donor-acceptor type organosilicon polymers (**P6**) bearing oligothienylene and tetracyanobutadienylene units as the donor and acceptor units, respectively. These polymers exhibited red-shifted absorption bands at λ_{max} = 513–565 nm in UV-Vis spectrum, whose edges reached approximately 800 nm, indicative of the strong charge-transfer interaction between electron donor and acceptor in the macromolecular backbone. These polymers also displayed solvatochromic behaviors. Specifically, the UV-Vis absorption maxima moved to the longer wavelengths with increasing solvent polarity. **P6** was photoactive because irradiation of TiO₂ electrodes in the polymer solutions resulted in the attachment of the polymer onto the TiO₂ surface via the formation of Si—O—Ti anchor bonds.

P6

Bu = Butyl

x = 3-5
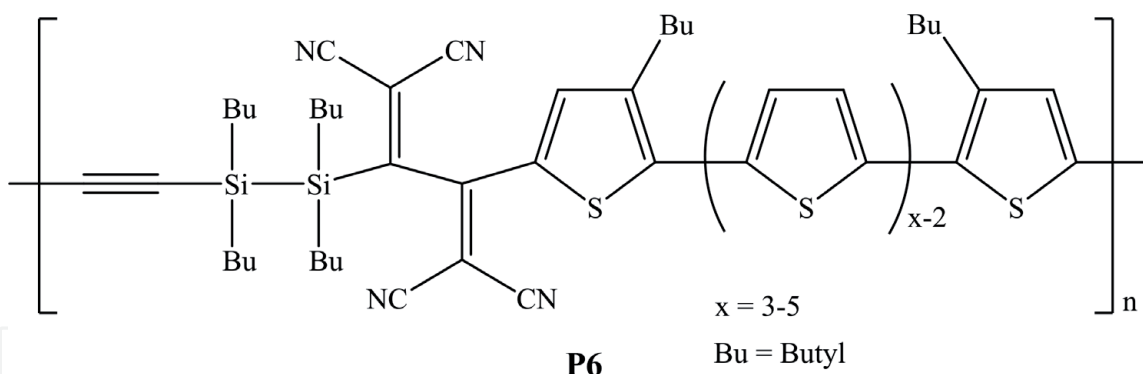
The cycloaddition/retroelectrocyclization reaction was first demonstrated in metal acetylide compounds [11], and thus metal-polyyne polymers may also be good candidates for the cycloaddition/retroelectrocyclization postfunctionalization to synthesize metal-containing donor-acceptor conjugated polymers. Yuan and Michinobu [37] synthesized a main-chain thiophene-based platinum-polyyne conjugated polymer, which was further reacted with TCNE to yield electron donor-acceptor polymer **P7**. The use of the thiophene and platinum (II) donors in the precursor polymer efficiently improved the reactivity of main-chain alkynes. As a result, **P7** was obtained under mild heating at 70°C. Moreover, this thiophene-based platinum (II)-polyyne precursor polymer was explored to react with TCNQ to afford **P8**. **P8** displayed stronger electron-accepting feature than **P7**, as revealed by the more bathochromically shifted charge-transfer band and the lower first reduction potential. In order to enhance the electron-withdrawing property of electron donor-acceptor polymers, diketopyrrolopyrrole and benzothiadiazole were incorporated into **P9** and **P10**, respectively [58]. The LUMO levels decreased significantly to about −4.2 to −4.5 eV after postfunctionalization with TCNE.


P7

P8

P9

P10
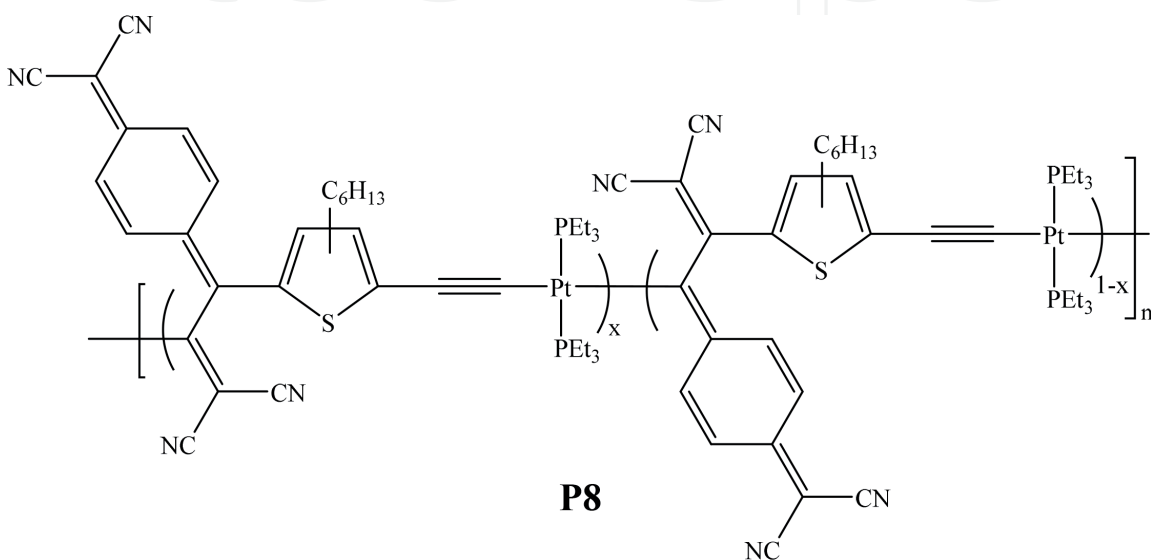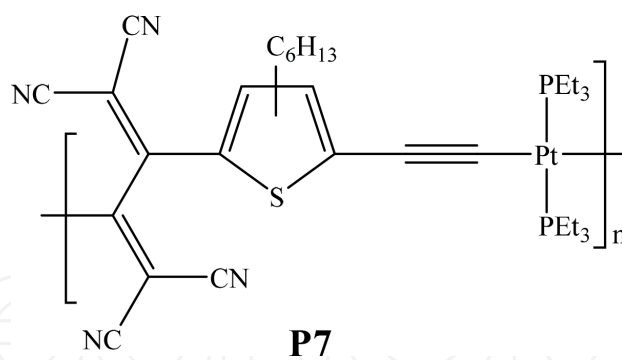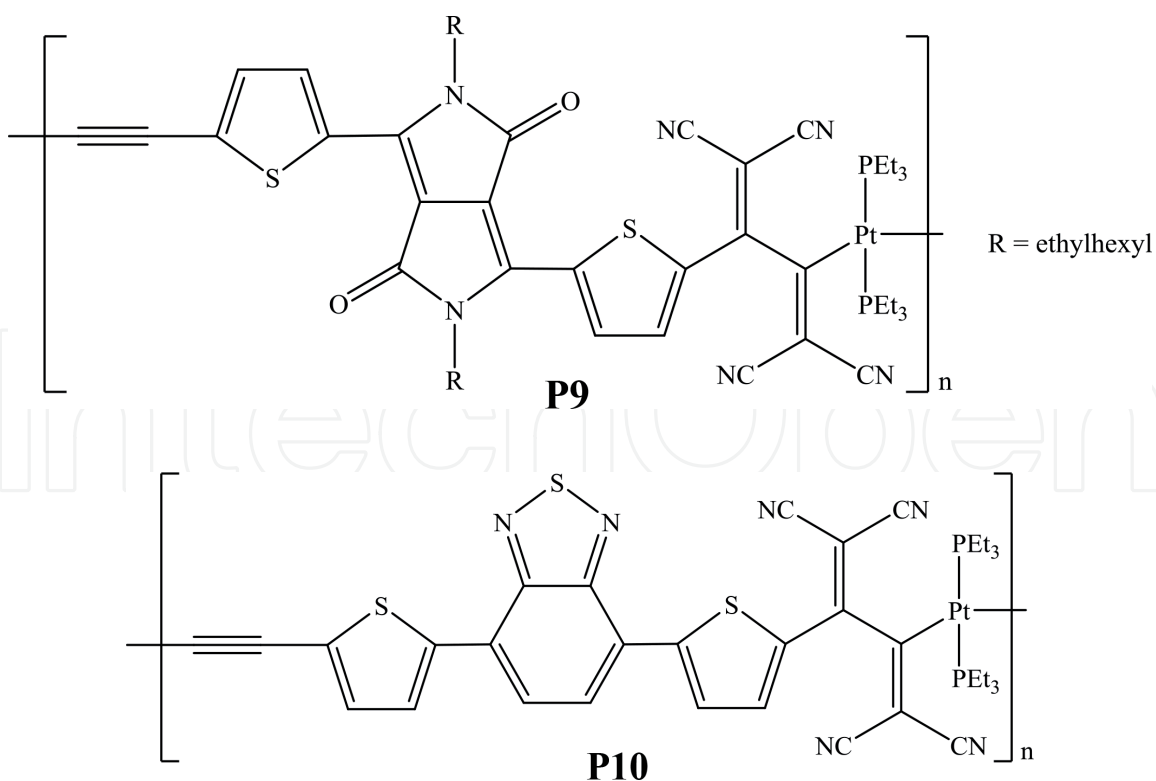
Huang [38] reported a facile synthetic route for synthesizing a main-chain donor-acceptor type polymer containing strong electron-donating dialkylamino groups and strong electron-accepting 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) units. The precursor polymer has a dialkylanilino group in the para-position on each main-chain alkyne, affording the strongest electron-donating effect for promoting the highest reactivity between TCNE and main-chain alkynes [36]. This molecular design overcomes difficulty in successfully implementing the postfunctionalization of main-chain ethynyl groups along the macromolecular chain in a complete manner. Specifically, an electron-donating monomer 4,6-diethynyl-N,N,N,N-tetrahexylbenzene-1,3-diamine was successfully synthesized by converting two carbaldehyde groups in the corresponding monomer into acetylene groups using lithium trimethylsilyldiazomethane via a Colvin rearrangement. This electron-donating monomer was then polymerized with a carbonyl-activated diiodide monomer to afford an electron-donating π-conjugated precursor polymer with a reasonably high molecular weight, which was further reacted with TCNE via cycloaddition/retroelectrocyclization reaction under mild conditions to afford the target polymer (**P11**). **P11** shows a very low bandgap energy (E_g^{opt} = 1.40 eV and E_g^{CV} = 1.10 eV), because of strong intramolecular charge-transfer interactions between electron donors and acceptors along the macromolecular chain.


P11
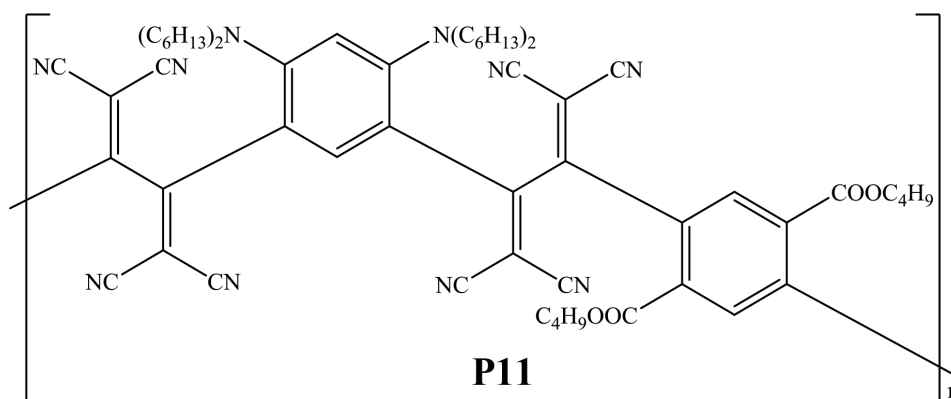
### 2.1.2 Main-chain electron donor-acceptor nonconjugated polymers

Washio and Michinobu et al. [39] reported postfunctionalization of TCNQ-containing polyester by cycloaddition/retroelectrocyclization reaction with a small-molecule aniline-activated alkyne to yield a polyester containing electron donor-acceptor chromophores (**P12**). **P12** possessed the colorimetric chemosensor ability, as evidenced by well-defined color changes of the charge-transfer band) due to the recognition of Ag^+ and Fe^{3+} ions. In contrast, the precursor TCNQ-containing polyester did not show any spectral changes upon the addition of Ag^+ and Fe^{3+} ions. Specifically, the Ag^+ ion was recognized by the cyano nitrogen atoms as a result of the effective multivalent coordination, leading to a bathochromic shift in the charge-transfer band. On the other hand, the Fe^{3+} ion was recognized by the aniline nitrogen atoms, as evidenced by the disappearance of the charge-transfer band.
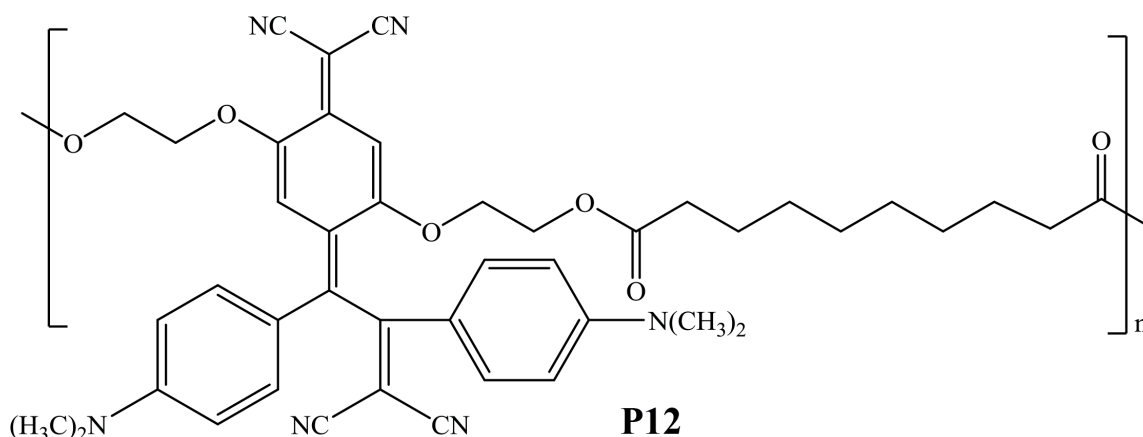
By using a similar method to the synthesis of **P12**, polymeric electro-optic materials (**P13**) were synthesized by simple heating of a mixed thin film of TCNQ-containing polyester and an aniline-activated dialkyne molecule to 140°C under electric poling [59]. A thermal addition reaction between electron-rich alkynes and TCNQ moieties enabled the formation of donor-acceptor chromophores as well as cross-linking networks throughout the polymer film to effectively fix the dipolar orientation induced by electrical poling. It took about 13 h to complete the reaction, and the electro-optic coefficient (d_{eff}) showed the maximum value of 0.609 pm/V after 2.5 h.
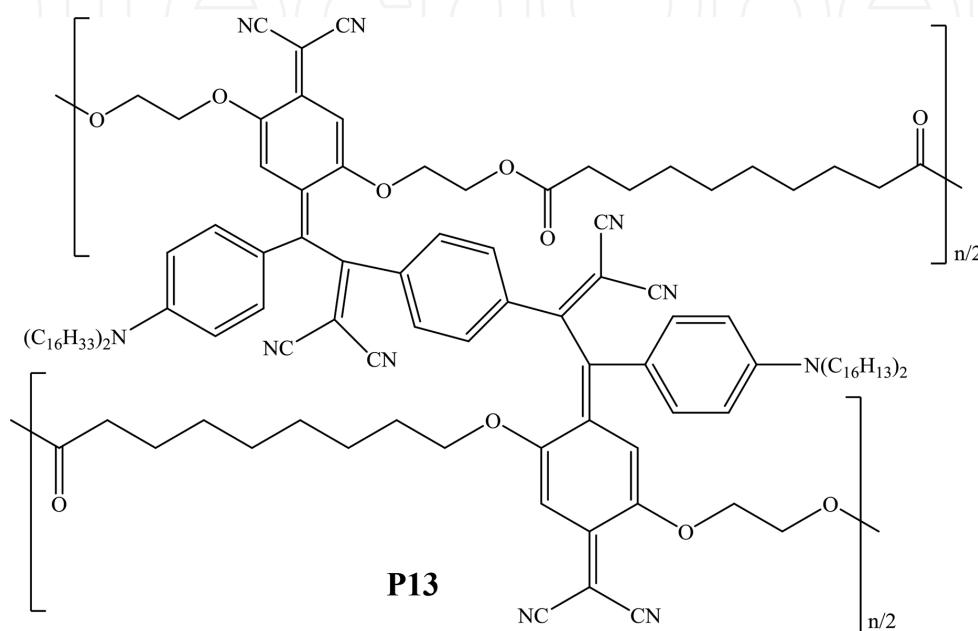
Washino and Michinobu [42] described the polyaddition polymerization between electron-rich alkynes and a TCNQ-containing molecule to yield electron donor-acceptor non-conjugated polymers (**P14**). The electron-donating monomer possesses two dialkylaniline-substituted alkynes, while the electron-accepting monomer contains two TCNQ moieties. The aforementioned two monomers were then reacted in 1,2-dichloroethane under mild heating conditions to produce the desired linear polymers with high molecular weights. It was reported that high molecular weight polymers were preferentially formed at high monomer concentrations; however, cyclic compounds dominated when the monomer concentration was low. In both cases, the degree of reaction could be readily monitored by observing the shift of the charge-transfer band in UV-Vis spectra. The presence of terminal groups in the polymers were determined by the cyclic voltammetry, demonstrating the linear polymer structures of **P14**. **P14** showed an excellent thermal stability with the decomposition temperature exceeding 300°C. It also exhibited strong charge-transfer bands and redox activities due to the produced donor-acceptor moieties.

P14
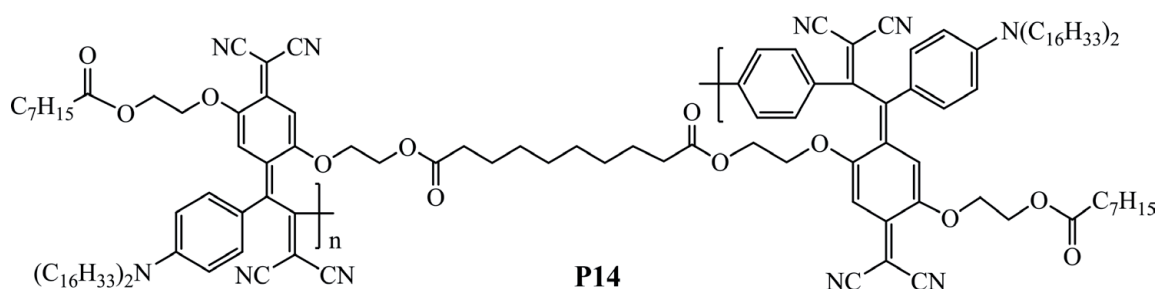
Furthermore, Washino and Michinobu [60] synthesized sequence-regulated linear polymers by multiple click chemistry reactions, which could include cycloaddition/retroelectrocyclization reaction along with other click chemistry reactions such as copper (I)-catalyzed alkyne-azide cycloaddition (CuAAC) and Diels-Alder cycloaddition to create electron donor-acceptor polymers. The orthogonality with CuAAC was explored by investigating the reaction orders. It was only possible to complete the metal-free double click reactions in the order of the Diels-Alder cycloaddition followed by the alkyne-TCNQ addition. The resulting donor-acceptor chromophores in **P15** gave rise to optical metal ion sensing, a colorimetric chemosensor behavior toward the Ag^+ ion and electrochemical properties.

P15
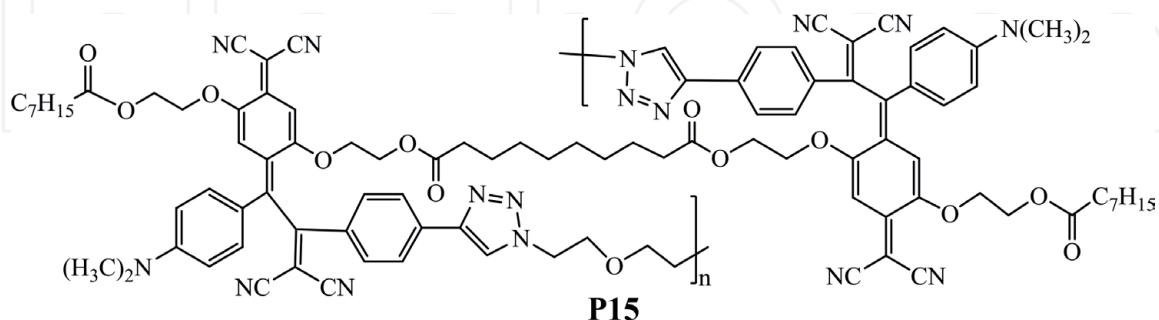
2.2 Side-chain electron donor-acceptor organic polymers

In contrast to main-chain alkynes, side-chain alkynes showed a reactivity as high as the corresponding small molecules, probably due to the lowered steric hindrance. Thus, the full TCNE addition to the polymer side chains could be achieved. Since click postfunctionalization does not require any tedious purification process, such as column chromatography and reprecipitation, a series of side-chain electron donor-acceptor polymers have been synthesized by this approach [40, 41, 61].

2.2.1 Side-chain electron donor-acceptor conjugated polymers

Michinobu [40] first synthesized a precursor polyamine bearing the electron-rich alkynes in the side chain, which was subsequently reacted with TCNE and TCNQ to give side-chain electron donor-acceptor conjugated polymers, **P16** and **P17**, respectively [62]. The successful addition of TCNE or TCNQ to the precursor polyamine was confirmed by the matrix-assisted laser desorption/ionization with time-of-flight (MALDI-TOF) mass spectra and the absence of the acetylene peak signals in the ^{13}C NMR spectrum. The π-conjugation length of **P16** and **P17** was enhanced in the presence of electron-accepting moieties, thus leading to red shifts in their absorption spectra and significant reduction in their bandgaps. As the TCNE or TCNQ addition increased, both glass transition temperature and thermal decomposition temperature of the polyamines gradually increased. For example, the increment in the glass transition temperature was 27°C, while the increase in the thermal degradation temperature was 118°C for **P16**. These authors successfully fabricated thin film transistors based on **P16** and **P17** and established a clear correlation between the polymer energy levels and hole mobilities [63]. By using a similar strategy, a triphenylamine-based conjugated polymer (**P18**) with cyano-containing chromophore in the side chain was synthesized and used for probing Hg^{2+} ion. Specifically, fluorescence of **P18** solution in tetrahydrofuran was specifically quenched by the introduction of I^-, accompanied by the change of its apparent color from pale brown to light yellow. In the presence of Hg^{2+} ion, the fluorescence of **P18/I—** complex recovered very quickly and even exceeded the initial intensity of pristine **P18** [64].


P16

P17

P18
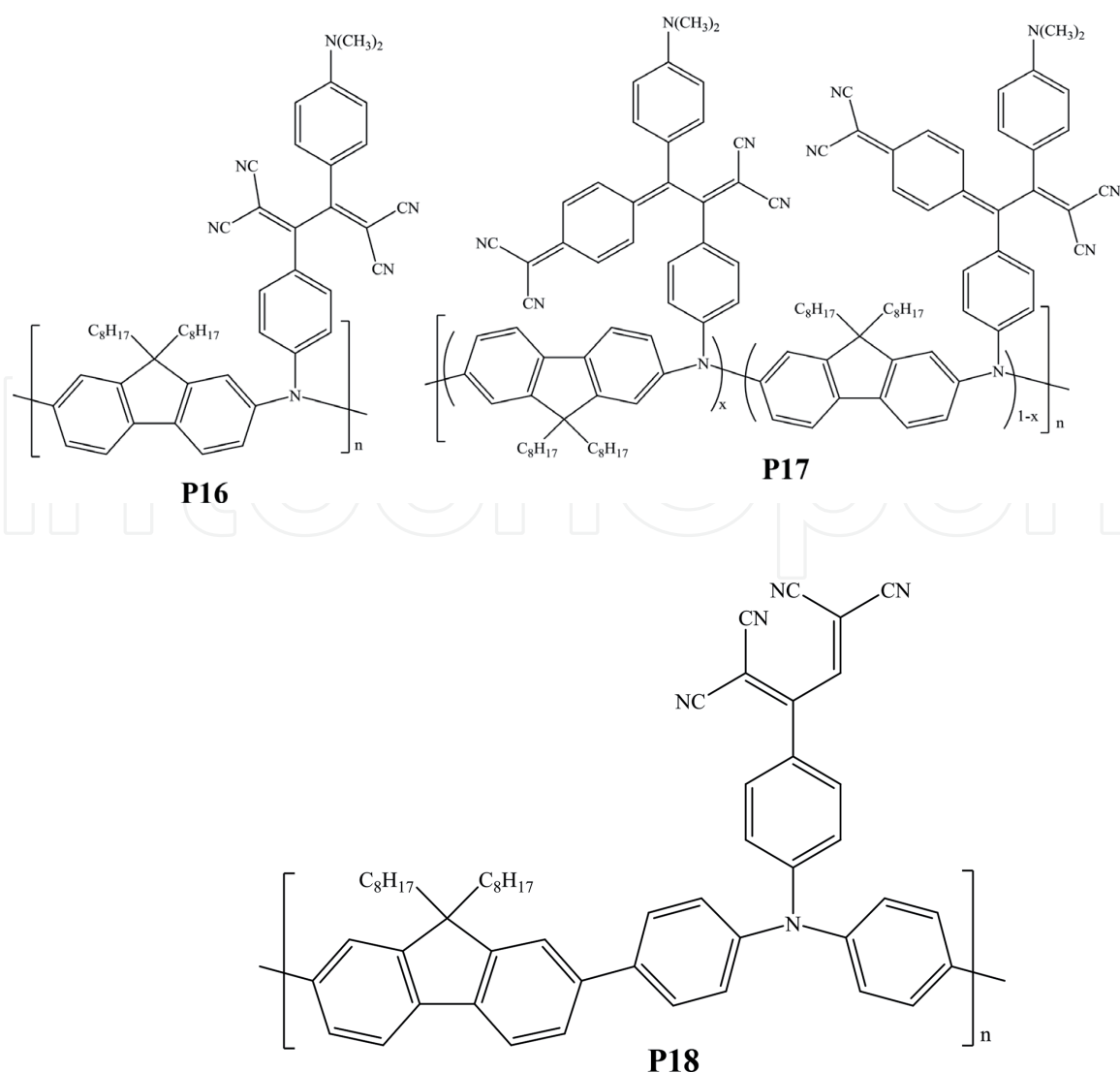
The click postfunctionalization of side-chain donor-acceptor conjugated polymers has been leveraged to other conjugated polymer systems, such as polythiophene, poly(p-phenyleneethynylene), and poly(phenylacetylene) derivatives. Yuan et al. [61] reported the synthesis of a polythiophene electron donor-acceptor polymer **P19**. The reaction started from the highly region-regular poly(3-hexylthiophene) prepared by the Grignard metathesis polymerization, bromination at the 4-position of the thiophene ring, and Stille coupling reaction, to TCNE addition to the side-chain alkynes. Chemical and electrochemical n-doping of the TCBD moieties of **P19** resulted in the formation of poly(radical anion)s and poly(dianion)s. The temperature-dependent magnetic measurements were used to characterize the high spin state of the poly(radical anion)s, because regioregular polythiophene is classified as a non-Kekule and non-disjoint connectivity [61]. Furthermore, a regio-irregular polythiophene derivative with dialkylanilino-substituted alkyne side chains was synthesized by the Suzuki polycondensation, and then it was reacted with TCNE and TCNQ to afford **P20** and **P21**, respectively [65]. The study on the poly(phenylacetylene)-based electron donor-acceptor polymers (**P22**) indicated that the click postfunctionalization had a significant impact on the intermolecular interactions [29, 66]. Upon the completion of cycloaddition/retroelectrocyclization click postfunctionalization of the precursor polymer with TCNE, the film morphology changed from an unstructured homogeneous surface to fibrous nanostructures. As a result, the diffusion coefficients of O_2 and N_2 were dramatically reduced, which was attributed to the decrease in the void spaces. Wang et al. [67] synthesized a series of poly(p-phenylenebutadiynylene) electron donor-acceptor polymers (**P23**), which were prepared by homocoupling polymerization of asymmetric bifunctional monomers, followed by the "click" chemistry with TCNE to introduce donor-acceptor chromophores in the side chain. The energy level and bandgap could be precisely controlled by the addition of acceptor molecules, as evidenced by the optical and electrochemical characterizations.

P19　　　　　　　　　　　**P20**

P21　　　　　　　　　　　**P22**
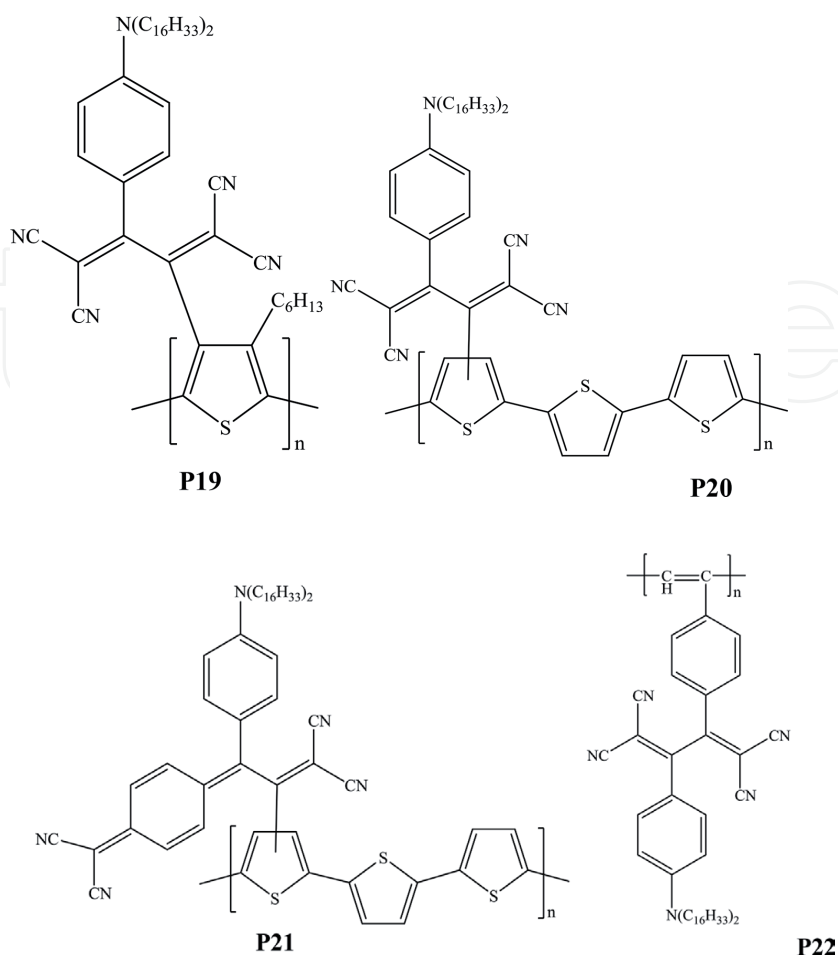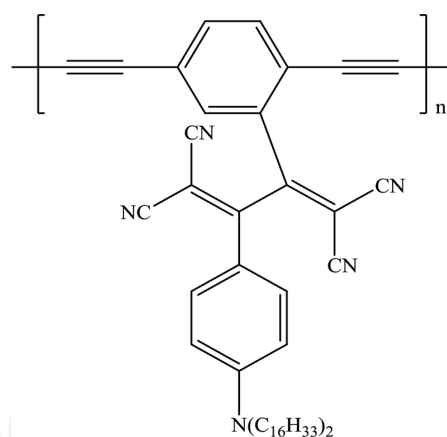
P23

Huang and Chen [41] developed an effective approach to synthesizing a low bandgap poly(arylene ethynylene) (**P24**) having donor-acceptor type chromophores in both side chains. Specifically, a diacetylene monomer and a carbonyl-activated diiodide monomer were synthesized and then polymerized by palladium-catalyzed cross-coupling reaction to afford a π-conjugated precursor polymer, which has approximately 50 repeat units of alternating arylene and ethynylene. The dioctylanilino-activated alkynes in the side chains of the precursor polymer were able to selectively react with TCNE by click-type [2+2] cycloadditions and the subsequent retroelectrocyclization to form the donor-acceptor type chromophores. The deactivated alkynes in the main chain of the precursor polymer remained intact so that the unique features of poly(arylene ethynylene)s such as excellent thermal stability and photostability could be kept in the target polymer. This unique polymer exhibited strong intramolecular charge-transfer interactions as evidenced by UV-Vis spectroscopy and cyclic voltagrammetry. As a result, **P24** has a low bandgap energy (E_g^{opt} = 1.59 eV and E_g^{CV} = 1.35 eV) and enhanced thermal stability.
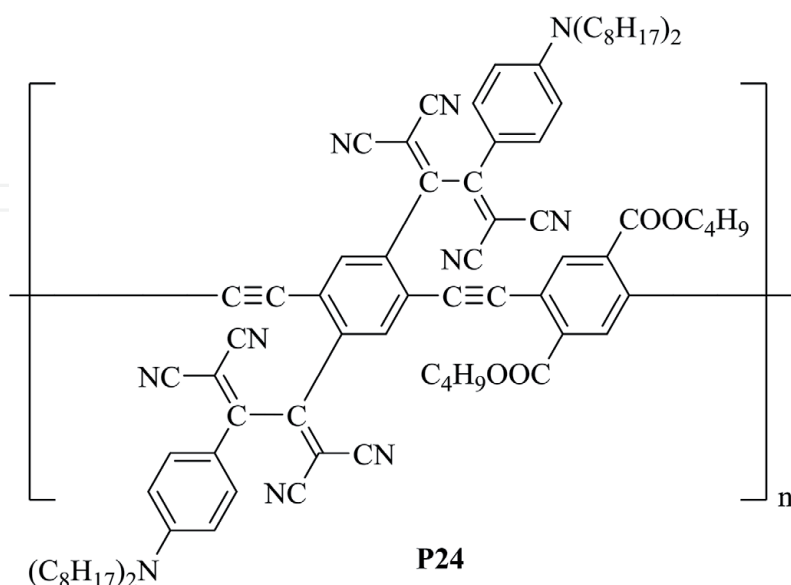

P24

2.2.2 Side-chain electron donor-acceptor nonconjugated polymers

Polystyrene-based polymers bearing dialkylanilino-substituted alkynes in the side chain are an important family of precursors for synthesizing electron donor-acceptor nonconjugated polymers by cycloaddition/retroelectrocyclization reaction. The "click" type reaction of TCNE and TCNQ with these

polystyrene-based precursors afforded the corresponding new materials (**P25** and **P26**) bearing electron donor-acceptor moiety in the side chain [46, 47]. Both **P25** and **P26** displayed well-defined charge-transfer bands in the visible region at ca. 480 and 730 nm, respectively, which enabled the visual detection of analytes. Specifically, **P25** selectively detected Fe^{3+}, Sn^{2+}, and Fe^{2+} ions, while **P26** preferred Fe^{3+}, Sc^{3+}, Ti^{4+}, and Cu^{2+} ions. The decrease in the charge-transfer band in the visible–near-infrared region was a result of the recognition of these metal ions by anilino nitrogen atoms in the side chain of **P25** and **P26**, and thus discoloration was a sign for visual recognition. On the other hand, only the Ag^+ ion could interact with the cyano groups in the side chains of polymers through the multivalent coordination. As a result of this interaction, a bathochromic shift occurred in the charge-transfer bands, leading to the change of the visual colors.

P25   **P26**
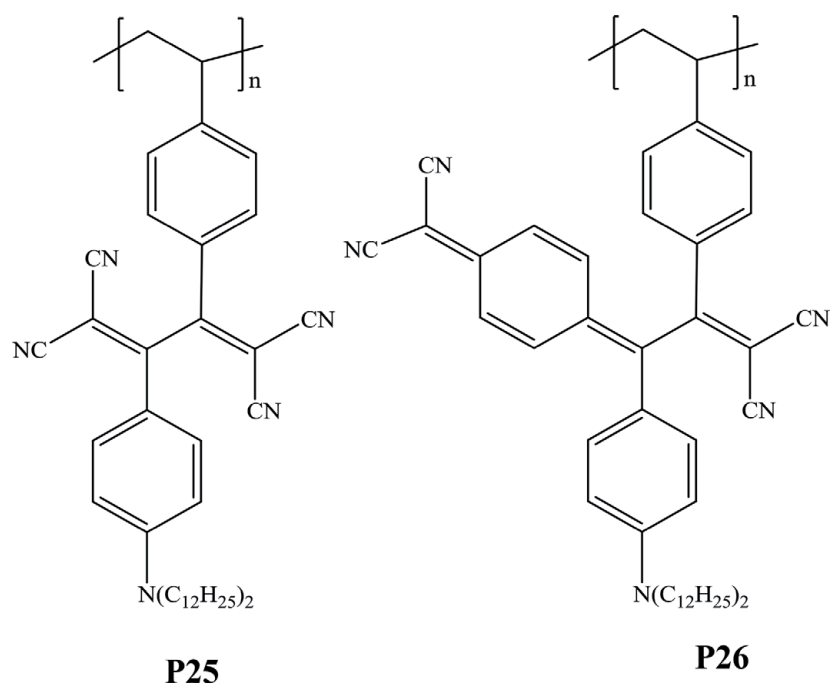
The orthogonal reactivity is one of the key features of click reactions. In order to illustrate the orthogonal reactivity of the cycloaddition/retroelectrocyclization reaction, double click postfunctionalization of poly(4-azidomethylstyrene) was conducted by CuAAC, followed by a cycloaddition/retroelectrocyclization reaction with TCNE or TCNQ to yield polymers, **P27** and **P28**, respectively [64, 68–72]. It should be noted that both click reactions proceeded rapidly without any side reactions, and carrying out the reactions in the reverse order also gave the same products. Upon the completion of electric poling, the second-order nonlinear optical responses of the polymer films were observed. Furthermore, all these polystyrene-based electron donor-acceptor nonconjugated polymers exhibited very specific colorimetric ion sensing behaviors [73–76]. The hard basic aniline nitrogen atoms preferred to interact with hard acidic metal ions like Fe^{3+}, leading to the decrease in the charge-transfer absorption band and thereby resulting in decolorization. On the other hand, soft basic cyano nitrogen atoms selectively captured the soft acidic Ag^+ metal ion, which caused a bathochromic shift of the charge-transfer band wavelength, thus leading to well-defined color changes. Nevertheless, the recognition of Ag^+ ions by the cyano groups was not possible for the corresponding monomeric electron donor-acceptor molecule, which was attributed to the fact that multiple cyano coordinations were essential for the selective recognition of the Ag^+ ions.

P27 **P28**
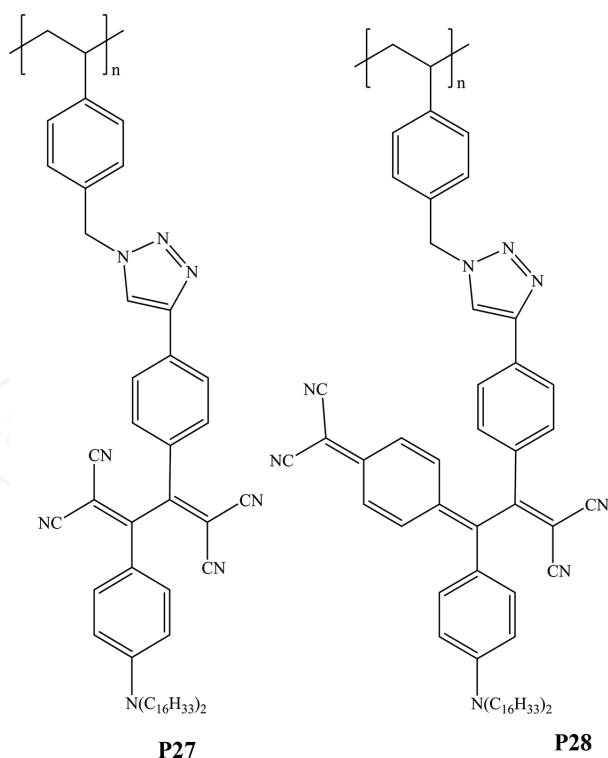
Atom transfer radical polymerization (ATRP) of N,N-didodecyl-4-[(4-vinylphenyl)ethynyl]aniline was conducted with bromine-terminated polystyrene to synthesize block copolymers composed of unsubstituted polystyrene and electron-rich alkyne functionalized polystyrene segments. These block copolymers were then reacted with TCNE to introduce electron donor-acceptor chromophores into the side chains of polymers to produce TCNE-adducted polymers (**P29**). **P29** exhibited intense charge-transfer bands, well-defined redox activities, and good thermal stability. In addition, polymer thin films based on **P29** were prepared by spin coating on a glass slide. The second harmonic generation (SHG) of these thin films was measured before and after electric poling. The results showed that the SHG coefficient (d_{33}) of the poled thin film was as high as 3.0 pm/V [70].

P29
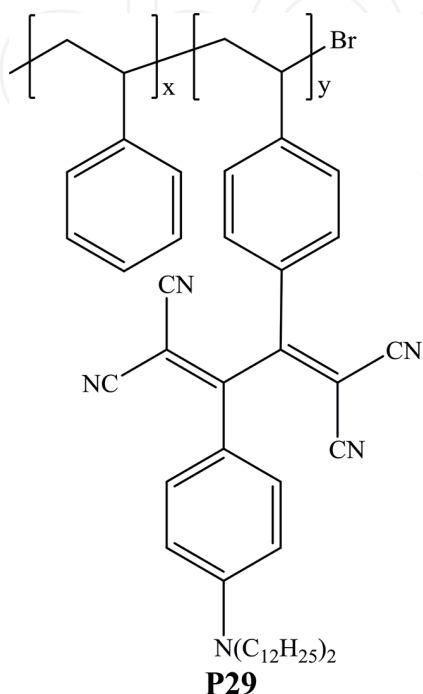
Fujita et al. reported the synthesis of a block copolymer (**P30**) by combining living polymerization techniques and cycloaddition/retroelectrocyclization reaction [77, 78]. This block copolymer contains a poly(3-hexylthiophene) block and a polystyrene block with an electron donor-acceptor chromophore. **P30** was used as an interfacial compatibilizer for P3HT/PCBM (herein, P3HT = poly(3-hexylthiophene), and PCBM = phenyl-C61-butyric acid methyl ester) bulk-heterojunction organic photovoltaic cells in order to facilitate the nanophase separation of each semiconducting domain. The TCBD moiety in polystyrene block of **P30** had higher affinity to the n-type semiconducting domain, while poly(3-hexylthiophene) block in **P30** had good compatibility with poly(3-hexylthiophene) p-type polymer. Under the optimized blend ratio of the block copolymer, the power conversion efficiency was enhanced, which was attributed to the increased short-circuit current and fill factor. Also, the crystallinity of poly(3-hexylthiophene) polymer was improved upon the addition of **P30**. The efficient compatibilizing performance of **P30** at the interface of P3HT/PCBM enlarged and fixed the interfacial area and in turn suppressed the recombination of the generated carriers.

P30
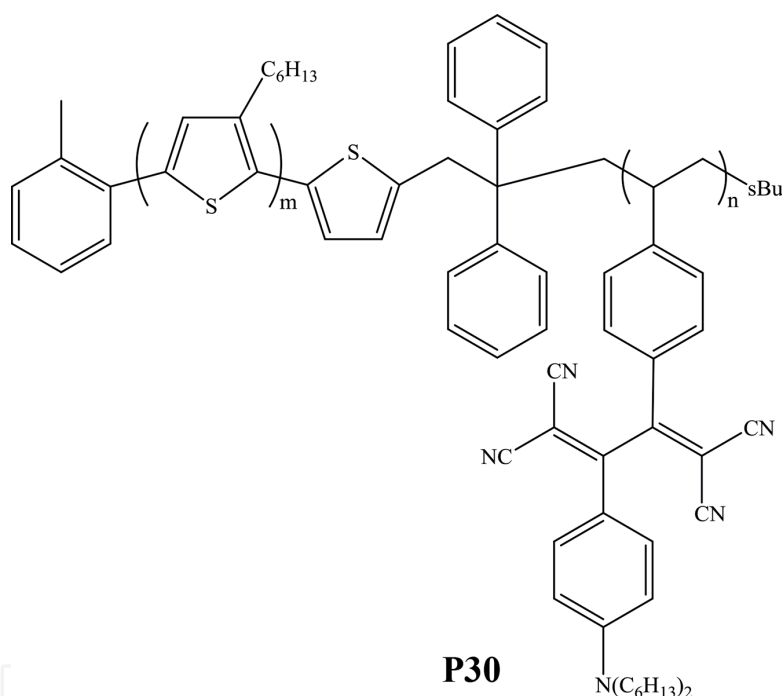
The combination of cycloaddition/retroelectrocyclization "click" chemistry and specific Ag$^+$ ion recognition was later leveraged to create multicolored polyurethanes [79]. Specifically, a colorless polyurethane derivative having electron-rich alkynes substituted by dialkylaniline donors at both sides was synthesized by polyaddition between a diol monomer and tolylene-2,4-diisocyanate. The side-chain alkynes in the precursor polyurethane were then reacted with TCNE and TCNQ to yield orange-colored and green-colored polymers, **P31** and **P32**, respectively. **P31** and **P32** exhibited the intramolecular charge-transfer bands centered at 476 nm and 698 nm in CH$_2$Cl$_2$, respectively. After complexation of Ag$^+$ ion with cyano groups in the side chains of **P31** and **P32**, the colors of the postfunctionalized polyurethanes were further changed. This was related to the change of the strengths of the intramolecular donor-acceptor interactions. For example, the solution color of **P31** changed to magenta and that of **P32** to a yellowish-green upon the Ag$^+$ ion addition. Furthermore, the electrochemical oxidation of the precursor polyurethane at >+ 0.25 V (versus Ag/AgCl in MeCN) gave a blue polymer. This color change was attributed to the formation of aromatic amine-based radical cations.

P31

P32
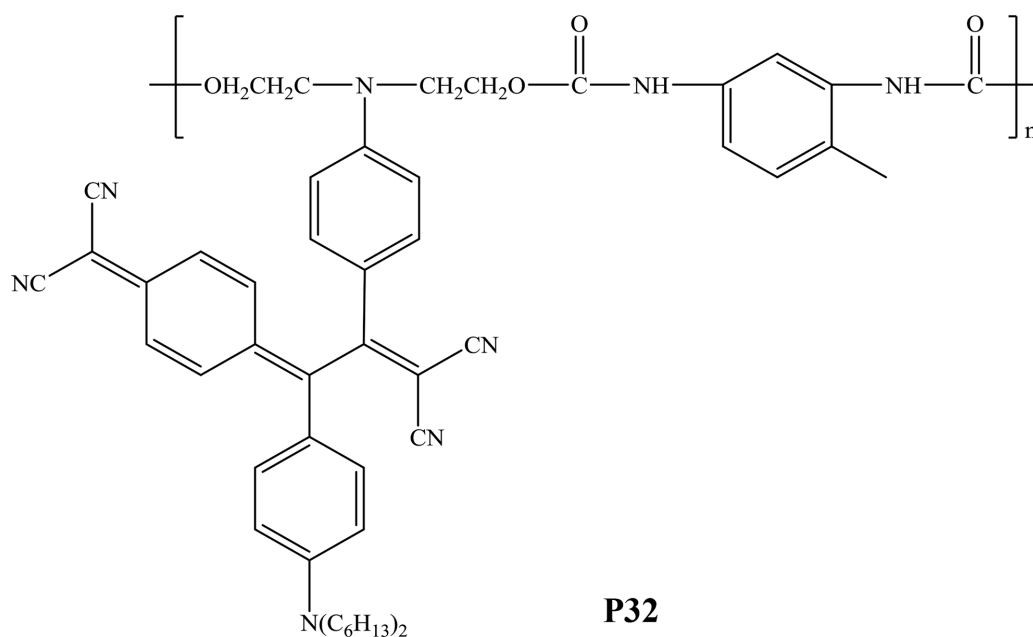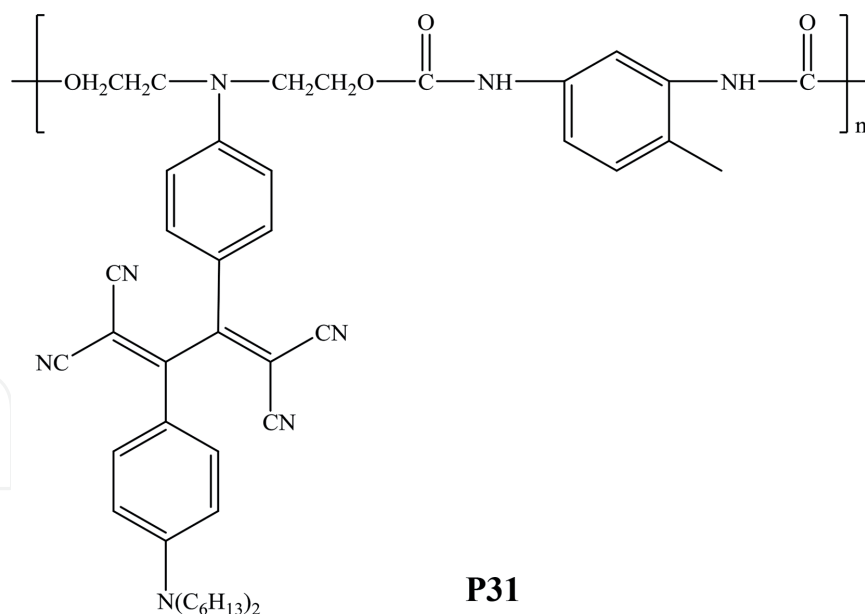
3. Summary and perspectives

This chapter gives an overview of electron donor-acceptor organic polymers synthesized by the "click" type cycloaddition/retroelectrocyclization reaction between electron donor-activated alkynes and olefinic acceptors such as TCNE and TCNQ. This "click" chemistry has many unique characteristics including high yields, short reaction times, and without the need for a catalyst or even a solvent. The salient features of the resulting electron donor-acceptor polymers encompass strong intramolecular charger-transfer interactions with tunable electronic absorptions that extend into the near-infrared region, active redox behavior, potent electron acceptor characteristics, high third-order nonlinear optical properties, high thermal stability, good solubility, and sublimation without decomposition, thereby enabling the preparation of thin films by vapor deposition. These electron donor-acceptor moieties have been integrated into the main chain or the side chain of polymers. In particular, the narrower bandgap and unique electrochemical properties of the resulting electron donor-acceptor conjugated polymers showed great potential in various applications such as nonlinear optical devices, organic photovoltaic devices, and light-emitting diodes.

This "click" chemistry was also effective for the synthesis of functional polymers with beautiful colors and successfully furnished the ion sensing abilities by the nonplanar donor-acceptor chromophores. Chemosensors are mainly classified as colorimetric and fluorometric sensors. However, chemosensors with a dual detection ability are very rare. Nonconjugated polymers bearing side-chain electron donor-acceptor chromophores composed of dialkylanilino donor and cyano-based acceptor groups have demonstrated the dual colorimetric detection behavior of several metal ions based on the specific interactions with different nitrogen atoms. Hard to borderline metal ions, such as Fe^{3+}, Fe^{2+}, and Sn^{2+}, are always recognized by the dialkylanilino nitrogen atom, resulting in a decrease in the charge-transfer band intensity of the donor-acceptor chromophores. On the other hand, the recognition site of a soft metal ion of Ag^+ is the cyano nitrogen atom due to the readily formed multivalent coordination which produces formed multivalent coordination leading to the bathochromic shift of the charge-transfer band. Chemosensors that can detect specific metal ions based on ligand-metal interactions have attracted increasing attention because of their high selectivity and low cost compared to other precise analytical techniques, such as atomic absorption spectroscopy and mass spectrometry.

The successful stories of electron donor-acceptor polymers enabled by the cycloaddition/retroelectrocyclization "click" chemistry open up a new avenue toward the synthesis of advanced polymers such as low bandgap polymers, intrinsically molecule-based conductive and/or magnetic polymers, organic photovoltaics, molecular batteries, and many other future applications.

Author details

Wenyi Huang
E.I. du Pont de Nemours and Company, Midland, MI, USA

*Address all correspondence to: wenyi.huang@dupont.com

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