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Polypyrrole Derivatives for Electrochromic Applications

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Electrochromic materials display reversible color change upon electrochemical cycling. Within the last two decades there has been growing interest in the electrochromic properties of polypyrroles. In this article, we highlight and provide insight about the electrochromic properties of polypyrroles in terms of their structure-property relationships without the intention of providing a complete chronological order.

1. Introduction

Chromism, which is described as the reversible change of material's color resulting from a electrochemical stimulus is called electrochromism. An electrochromic material undergoes reversible optical change (transmittance and/or reflectance) due to its electrochemically induced oxidation and reduction [1,2]. Coloration could take place between a transparent and a colored state, or between two colored states or between multiple steps (multichromic). Depending on the coloration type, these materials can be classified as anodically coloring (coloration upon oxidation) or cathodically coloring (coloration upon reduction). Starting from the first discovery [3] this phenomenon has been profoundly investigated by many researchers and developed in to a huge family which can be subdivided as metal oxides [4,5], molecular dyes [6,7] and conducting polymers [8,9]. Electrochromism has drawn a great deal of attention for its potential applications such as smart mirrors and windows, displays, active optical filters, data storage and camouflage material for military purposes [10]. However, commercialization of these materials depends on their switching times, optical contrast, coloration efficiency and long term stability.

Electrochromic contrast, which is often measured as the percent transmittance change ($\Delta\%T$) of the electrochromic material at a specific wavelength, is an essential parameter for characterization the electrochromic materials [11]. For applications such as smart windows, where the difference between the bleached and colored states is expected to be the highest, the electrochromic contrast is generally recorded on a wide range. For these applications, a bleached state with a transmission of at least 80% within the visible window is necessary. To convey more information on the perception of transmittance to the human eye, measurements on the relative luminance change during an electrochromic switch are also considered to be useful [12]. Basically, *switching time* (response time) is defined as the time needed to switch between the two extreme redox states of the electrochromic material. It is generally followed by a square wave potential step method coupled with optical spectroscopy. Depending on conductivity and solvation of the electrochromic material, ion diffusion within the film, the switching time of an electrochromic material could be in the order of several minutes to milliseconds. Additionally, magnitude of the applied potential, thickness and morphology of the film are known to be effective on switching characteristics. *Coloration efficiency* (CE), which basically defines the change in optical density per inserted charge, is a fundamental parameter for investigating the power requirements of an electrochromic materials. CE at a given wavelength (λ) can be calculated using the following equation [12]:

$$CE\ (\lambda) = \Delta OD(\lambda)/(Q/A) = \log[T_b/T_c]/\ (Q/A)$$

where $\Delta OD(\lambda)$ is the change in the optical density at λ_{max}, Q the inserted charge, A the electrode area, T_b and T_c are the bleached and colored transmittance values, respectively. The increase in CE generally indicates the more effective use of injected charge. *Stability* of electrochromic materials is generally reported as the number of redox cycles that a material stand without significant loss in the performance, which is related with the irreversible oxidation or reduction at extreme potentials, side reactions with water or oxygen and heat release in the system during switches. *Optical memory*, on the other hand, indicates the persistence of the color under open circuit conditions, which is of fundamental importance for electrochromic devices.

Since the discovery of the electrochromic effect by Deb[3] tremendous amount of studies were performed on metal oxides such as, WO_3, NiO, MoO_3, TiO_2, Ta_2O_5, Nb_2O_5 and mixed metal oxides[4]. The electrochromic response of these materials is based on reversible modulation of the oxidation states of the transition metal, which depends on injection of positive ions (H^+, Li^+, Na^+ and K^+) and electrons into multivalent transition metal oxide [5]. Among many metal oxides, tungsten oxide have been the most extensively studied due to its high coloration efficiency (typically greater than 50 $cm^2\ C^{-1}$) and stability [4]. The material is known for its cathodic coloration from colorless to blue, which could be prepared by techniques such as sputtering, thermal evaporation, sol−gel method etc. In recent years particular efforts have been devoted on nanostructured WO_3 with various surface morphologies such as nanoparticles, nanorods, nanowires etc. In general, nanostructured WO_3 exhibits promising switching times (below 5 s) and moderate coloration efficiency around 35 to 65 $cm^2\ C^{-1}$ [11]. Interestingly, having large active surface area and extensive grain boundaries, the electrochemically prepared nano-WO_3 revealed improved electrochromic performance, where an optical contrast of 88.51% and excellent coloration efficiency of 137 $cm^2\ C^{-1}$ were achieved [13]. Recently, composite materials based on conducting polymers and metal oxide nanostructures have been actively studied. Among those, composites of polyaniline and WO_3 revealed promising features showing color variation from dark blue at negative potentials to violet-green at positive potentials [10].

Almost 40 years ago polyacetylene, which is the simplest form of a conjugated polymer, was shown to reveal near metallic electrical conductivity upon chemical doping [14]. This breakthrough caused an explosion of an interdisciplinary research area; and the family of conducting polymers have tremendously grown upon chemical and/or electrochemical polymerization of aromatic molecules, such as pyrrole, thiophene, aniline, furan, carbazole etc. Although the original intention was to pursue their ability to conduct electricity, these materials were shown to have far more to offer in various applications. In fact the scientist, who triggered dawning of this new era were awarded with 2000 Nobel Prize in Chemistry *"for the discovery and development of conductive polymers"*.

Among conducting polymers, polypyrroles (PPy) is by far the most extensively studied polymer due to its low oxidation potential, water solubility and low cost of its monomer (pyrrole) [15]. Polypyrrole derivatives, in general, possess exclusive properties, such as moderate environmental stability, good redox properties and enhanced compatibility in aqueous systems, which pave the way for their utilization in numerous applications including batteries, supercapacitors, electrochemical sensors, mechanical actuators, electromagnetic interference shielding, drug delivery systems, optoelectronic devices.

For the synthesis of conducting polymers electrochemical polymerization is a frequently used technique since it requires small amount of monomer and it provides an effective platform that allows investigation of in-situ growing process of the polymer and further analysis by electrochemical and spectroscopic techniques. The technique is rather simple and it offers direct grafting of the intrinsically conducting polymer onto electrode surface without the need for subsequent doping process [16]. Despite the fact that polypyrrole was one of the first to be electrochemically synthesized, there is an ongoing controversy about its polymerization mechanism. Due to complexity of the film formation process and the lack of effective approaches for investigating the reaction kinetics, the reaction path is not crystal clear. Nevertheless, the mechanism is considered to entail formation of radical cation which is followed by either radical-cation/radical-cation coupling or reaction of a radical-cation with a neutral monomer. The mechanism (Fig.1) described by Diaz et al [17,18], which was later supported by the theoretical studies of Waltman et al. [19,20], is the most frequently referred mechanism in literature [21]. According to Diaz's approach following the first electrochemical step (E), which consists of the oxidation of the monomer into radical cation, the coupling of the two radicals cations results in formation of dihydro dimer-cation. Consecutively, the chemical step (C) occurs which leads to dimer, with the loss of two protons and re-aromatization. Due to extended conjugation over two rings, having lower oxidation potential than the monomer, the dimer oxidizes readily to form the radical cation (E) and undergoes coupling with a monomeric radical. Electropolymerization is proposed to proceed through to a general E(CE)n mechanism where consecutive electrochemical and chemical steps takes place until the oligomers become insoluble and precipitate onto the electrode surface [22]. However, further studies have shown the presence of many other competitive multistep reactions, and susceptible nature of the radical cation intermediates regarding the nucleophilicity of the polymerization medium [23].Typically, one electron is removed from the polymeric backbone for every three to four monomer units which results in the intrinsic electrical conductivity and provide a delocalized p-electron band structure. In the oxidized state, the polymer is charge balanced with anions, termed also as 'dopants', which are incorporated into the film to maintain electrical neutrality.

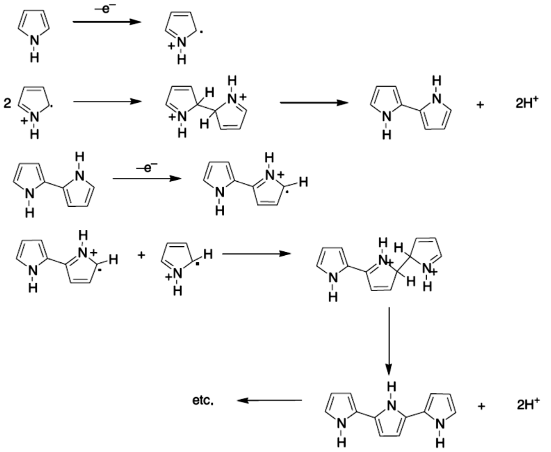

Fig.1 Proposed mechanism for electropolymerization of pyrrole by Diaz et al.

2. Band Structure and Electrochromism of Polypyrrole

Among the conducting polymers, polypyrrole was one of the first to be investigated for its optoelectronic properties whose electronic structure could be reversibly changed with doping [18]. Fig 2a represents the energy diagram of PPy in neutral form [24]. Having two-fold coordination, all conjugated polymers are susceptible to structural distortion. Upon oxidation (removal of π-electrons from the valence band) of neutral PPy, there occurs the local relaxation of the benzoid structure toward a quinoid-like, which creates radical cations (polarons) [25,26]. Formation of polarons induces two new energy levels (Fig 2b) that are symmetrically positioned within the bandgap. Thus, two new electronic transitions at longer wavelengths emerge. Further oxidation results in formation of bipolarons which are the charge carriers of the coupled cations (dication). Having lower energy state empty, bipolarons are signified by the broad, low energy

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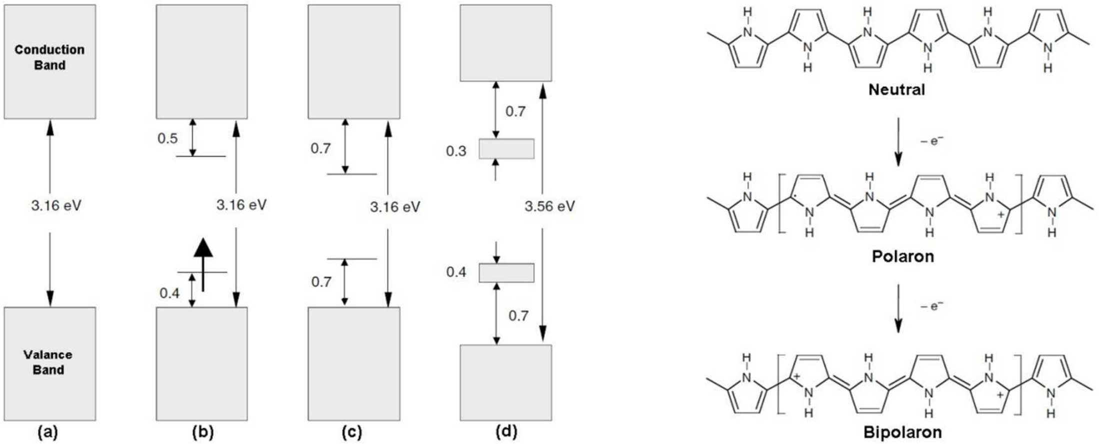


Fig.2 Electronic energy diagrams and structures for (a) neutral PPy, (b) polaron, (c) bipolaron, and (d) fully doped PPy [24].

absorptions due to the transitions from the top of the valence band (Fig 2c). As the polymer is oxidized further, the bipolaronic energy state overlaps and forms intermediate band structures as given in Fig 2d. Thus, the optical state (and the color) of the polymer is altered by creation of new electronic states (p- type doping) that result in the development of the lower energy absorptions. Fig 3. represents the spectral variations of PPy upon doping [27]. Potentially all the conducting polymers are electrochromic, which is based on creation and destruction of charge carriers (polarons and bipolarons) [28].

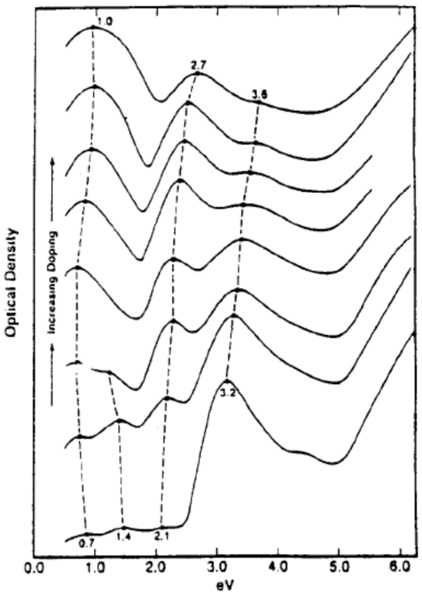


Fig.3 Optical absorption spectra of ClO_4--doped polypyrrole as a function of dopant concentration. The dopant level increases from the bottom curve (almost neutral polypyrrole) to the top curve (33 mol % doping level) [27].

Until now, immense efforts have been devoted to comprehend the underlying factors that contribute to the bandgap of these polymers. The energies related to the bond alternation ($E^{\Delta r}$), the mean deviation from planarity (E^{θ}), the aromatic resonance energy (E^{Res}), the inductive and mesomeric electronic effects of substituents (E^{Sub}) and the interchain interactions (E^{Int}) are shown to play part on the bandgap of conjugated polymers [29], where the bandgap is expressed to be; $E_g = E^{\Delta r} + E^{\theta} + E^{Res} + E^{Sub} + E^{int}$. Thus, by diverging the electronic nature of the polymer backbone and controlling the interchain interactions, the bandgap and ultimately the coloration of all conducting polymers could be modified. Polymers with E_g greater than 3.0 eV are generally termed as anodically coloring since they are colorless at neutral state, while absorbing (colored) in the visible region at the oxidized state [30] . On the other hand, those with E_g less than 1.5 eV serve as cathodically coloring materials which are colored in neutral state. Polymers with intermediate gaps show distinct color changes throughout the visible region such as polythiophene (E_g=2.0 eV, red to blue). The band gap could be categorized as optical and electronic bandgap. The former bandgap refers to the energy difference between the valance band and conduction band which is determined though spectroscopic techniques. Rather than demanding approaches such as Tauc plot etc. optical bandgap of the electrochromic polymers is readily determined from the low-energy absorption edge of the electronic absorption spectrum. The electronic bandgap, on the other hand, is measured through electrochemical methods, which is generally higher than the optical bandgap due to presence of electrode-film interface charge barrier. Following the determination of the onset of oxidation and reduction potentials of the polymer and comparing these values with a reference compound, HOMO and LUMO energy levels and subsequently, the electrochemical band gap of the polymer are calculated [22,29].

The optical bandgap of PPy is reported to be ~2.7 eV [18], whereas its electronic band gap is calculated as 3.15 eV [24].

The polymer appears yellow-green and blue-gray in its neutral and oxidized forms, respectively (Fig 4). The polymer has the tendency to degrade upon repetitive switching and only the extremely thin films of the polymer could be completely de-doped. Nevertheless, polypyrrole derivatives with improved electrochromic properties are available with tailor-made functionalization of repeat units, since the coloration in the conducting polymers mainly depends on the bandgap and its band structure.

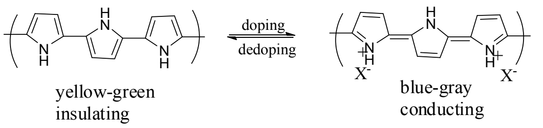


Fig.4 Electrochromism in polypyrrole.

An ideal electrochromic material is expected to have high optic contrast between its extreme states, a short response time and high stability. In conducting polymers, the rates of color change mainly rely on the rate at which the doping-dedoping process occurs. Since redox switching of conducting polymers is based on transfer of ions, the rate of color change mainly depends on both the morphology of polymer and polymer-electrode interactions. Towards understanding the effect of dopant ions, Girotto et al. added indigo carmine, an inherently electrochromic, redox active material having dianionic character, during electrochemical polymerization of pyrrole in the presence of dodecylsulfat [31]. The resultant polymer revealed higher coloration efficiency (137 cm^2/C) and optical contrast (37%) compared to polypyrrole/dodecylsulfat at 700 nm. Both dodecylsulfat and indigo carmine doped polypyrroles displayed pale yellow (in neutral state) and dark blue color (in oxidized state). Furthermore, the effect of utilization of azo (Remazol Black B) and anthraquinone (Dianix Red) dyes was investigated [32]. The former and the latter dye doped polypyrroles revealed electrochromic efficiency of 175 and 100 cm^2/C, respectively. Moreover, studies showed that polypyrroles synthesized in the presence of Remazol Black B and Dianix Red dyes revealed shorter switching times which was considered to be due to the enhanced mass and electronic transport with the formation of ‘‘nano-channels’’. Recently, similar type of studies were conducted where the electrosynthesis and the spectroelectrochemical characterization of eriochrome cyanine R doped polypyrrole was performed [33]. The dye doped polymer revealed enhanced optoelectronic properties relative to pristine PPy in terms of its optical contrast (27%) and switching time (less than 1.5 s). Yamada et al. investigated the electrochromic properties of PPy on Au nano-brush electrodes in order to enhance the switching time and life time of PPy [34]. Such approach was deliberately chosen (Fig 5) to improve the mass supply from the bulk of the solution and to compensate the adverse effect of volume change of the copolymer (deterioration of the adhesion between the polymer film and electrode) during switching. PPy films immobilized on Au nano-brush electrodes showed higher coloration efficiency and switching stability when compared to the PPy films on the Au planar electrode.

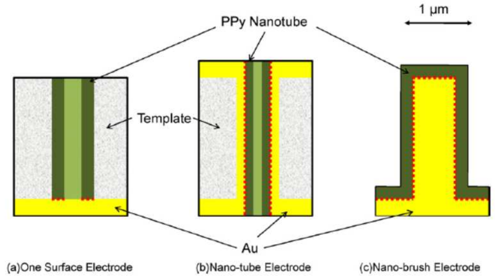


Fig. 5 Schematic diagrams for differences in the electrode configurations and the effective contacting area between the Au electrode and polypyrrole nano-tubes. Dotted lines indicate the effective contact surface. (a) One surface electrode; (b) nano-tube electrode; (c) nano-brush electrode [34].

Hybrid and composite materials represent an important class of materials which are expected to combine the merits of its constituents such as; flexibility, short response time, stability etc.

In 1988 electrochromic composite films of polypyrrole and phosphotungstate was prepared through electropolymerization of pyrrole in aqueous solutions which contain the sodium salt of phosphotungstate. Since PPy and phosphotungstate switch at different potentials, the composite film switched from yellow to red and finally to blue upon oxidation, showing typical coloration behavior of both PPy and phosphotungstate [35]. On the other hand, another organic–inorganic hybrid material, nickel oxide/polypyrrole (NiO/PPy) thin film showed enhanced switching time (0.601 s for coloration and 0.395 s for bleaching) and coloration efficiency ($358 cm^2/C$) compared to pristine PPy and NiO [36]. Most importantly, NiO/PPy presented a dramatically improved electrochemical stability (from about 500 switches for PPy to 10,000 switches for NiO/PPy) in contrast to PPy. Recently, Takagi et al. formulated a nanohybrid film where PPy was photoelectrochemically synthesized from the pyrrole monomer which was attached on to TiO_2 surface [37]. The response time of the nanohybrid film was found to be significantly slower than that of the PPy coated on a typical FTO electrode. By reducing the polymer thickness and using the fast electron transport property of the TiO_2, the nanohybrid film revealed the fastest reduction response time of 0.4 ms. Interestingly, PPy-poly(ethylene-co-vinyl alcohol)(EVOH) composite films, which were prepared by electrochemical polymerization of pyrrole on lithium perchlorate containing EVOH matrices, changed color reversibly from yellow to brown with markedly improved durability against the repeated application of potentials [38]. In another study, stability of PPy was enhanced through introduction of a triblock copolymer, poly(ethylene glycol) – poly(propylene glycol) – poly(ethylene glycol), into the oxidant solution during vapor phase polymerization process[39]. The resultant PPy demonstrated 20-fold increase in electrical switching stability compared to pristine PPy. In an another effort to achieve improved properties [40], carbon nanotube (CNTs) functionalized poly(N-methylpyrrole) was electrochemically synthesized in hydrophobic ionic liquid and a single layer electrochromic device was constructed with SnO_2:F counter electrode. The coloration of the device was from dark brown to pale yellow with an unstable transient green color. The device exhibited high cycle life and optical transmission (at 550 nm) of 69 % and 44 % in bleached and color state, respectively.

3. Tuning of Electrochromic Properties of PPy

3.1. Copolymerization

Controlling the bandgap of the polymer through structural modification, copolymerization, blending and lamination are the techniques that are applied to tune the color of the conducting polymers [41]. Copolymerization is an easy, facile approach to unite the distinct properties of the comonomers which might lead to exciting combination of the properties possessed by the corresponding homopolymers. In a work of Ak et al. [42], enhancement of electrochromic properties of PPy was achieved by electrochemical copolymerization of pyrrole with octa(thiophenephenyl)silsesquioxane (OPS). The copolymer (OPS–PPy) revealed multichromic behavior showing color change from yellow, red, gren-gray, blue. OPS–PPy switched more rapidly (0.4 s) compared to PPy (1.1 s) and revealed a noticeable increase in the optical contrast (Fig 6) (from 17% to 30% at 730 nm). Such an improvement was attributed to the loose packing of the PPy chains due to presence of OPS units, leading to more accessible doping sites and the facile ion movement during the redox switching. In a recent work [43], copolymerization of pyrrole with 3,4-ethylenedioxythiophene (EDOT) was performed in boron trifluoride diethyl etherate. The maximum absorption wavelength of π-π* transition was blue-shifted (from 462 nm to 556 nm) with the increase in the EDOT content of the feed. Resultant copolymers exhibited bandgaps between 1.71 to 1.64 eV. On the other hand, copolymers based on pyrrole and EDOT were synthesized in aqueous micellar solution with various feed ratio of pyrrole/EDOT [44].The copolymers synthesized at the feed ratios (pyrrole/EDOT) of 1/5 and 1/15, showed light brown to light blue and dark blue to light blue coloration upon doping, respectively. Compared to PPy, stabilities of the copolymers were improved presumably due to incorporation of EDOT units. Wen et al. [45] produced a pyrrole containing copolymer which was achieved through electropolymerization of pyrrole and 2,2'-dithiodianiline in propylene carbonate. UV-visible spectrum of the copolymer showed three optical transitions at λ_{max} 390, 540, and 800 nm for different applied potentials.

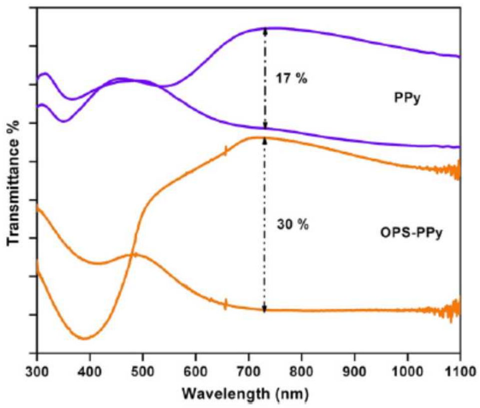
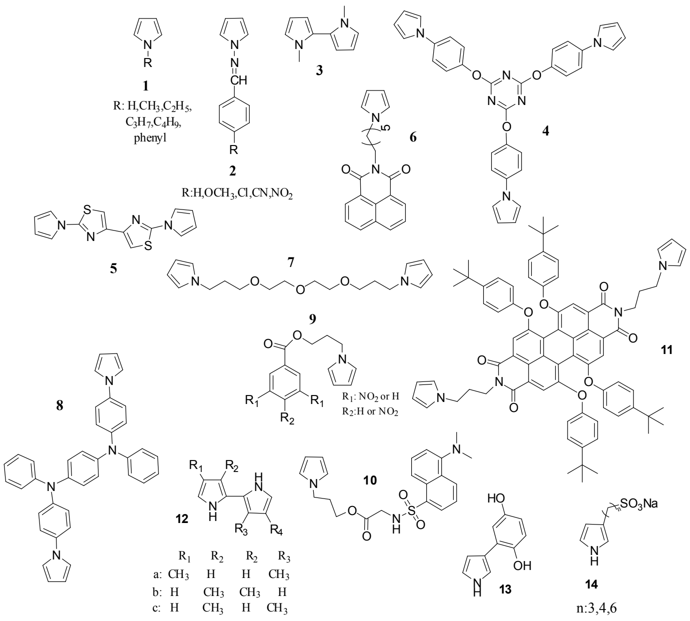


Fig. 6. Transmittance spectra of PPy and OPS–PPy in two extreme (oxidized and neutral) states [42].

3.2. Structural Modification

3.2.1. N- Substituted Pyrroles

While N-substitution on the pyrrole ring results an increase in the monomer oxidation potential and decrease in the polymer's conductivity, it provides immense synthetic opportunity for inclusion of various complex structures. Similar to unsubstituted PPy, poly(N-alkyl pyrrole)s (poly(**1**)) with various substituents from methyl (E_g = 2.7 eV) to butyl , to phenyl exhibited yellow to brown-black electrochromism upon oxidation [46]. On the other hand, PPys with various benzylideneamino groups (poly(**2**)) illustrated red to blue electrochromism upon oxidation [47]. Poly(N-methylpyrrole) synthesized through polymerization of the dimer (**3**) exhibited increased conductivity with a blue-shifted onset of absorbance at the neutral state [48,49]. Poly(**3**) was pale, transmissive yellow in the neutral state and gray-blue in oxidized state.



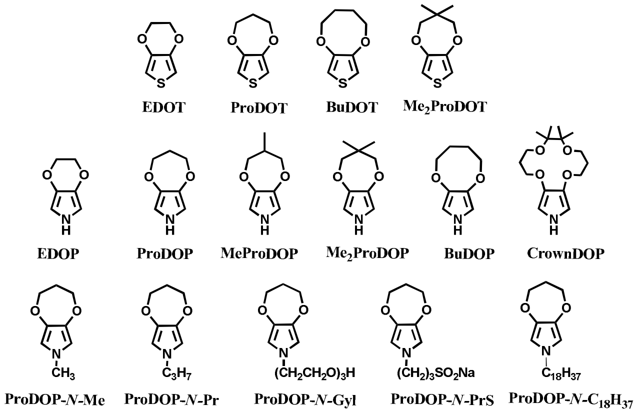
Another polypyrrole derivative which was synthesized through electrochemical polymerization of a star shaped, triazine containing monomer (**4**), displayed red and turquoise colors in fully oxidized and reduced states, respectively [50]. The optical bandgap of the polymer was found to be 2.97 eV. The polymer switched colors in 1.1 s and had an optical contrast of 20% (measured at 700 nm). Bithiazole containing pyrrole (**5**) derivative was electrochemically polymerized both in the absence and presence of EDOT [51]. The resultant polymers exhibited optical bandgaps ranging from 2.60 to 1.75 eV (depending on synthesis conditions). The multichromic copolymers revealed short switching times and useful optical contrast as 0.6 s and 54 %, respectively. Soluble, n-dopable, florescent, electrochromic polypyrrole derivatives were synthesized through both chemical and electrochemical polymerization of **6** [52]. The optical bandgap of poly(**6**) was calculated as 2.99 eV, 2.37 eV. The polymer exhibited a switching time of 1.63 s and an optical contrast of 33.37 %. An etheric member of N-linked polybispyrroles (poly(**7**)), on the other hand, appeared transparent yellow in the neutral state, light pink in the intermediate state, and blue in the oxidized state [53]. Poly(**8**) that contains triphenylamine derivative presented color variations form brown to blue in 0.6 s (95% of the full change) with an optical contrast of 52% (at 617 nm) [54]. Recently, two nitrobenzoyl pyrrole derivatives (**9**) were synthesized and subjected to electrochemical/chemical polymerization. The resultant polymers displayed color changes from pale green to dark grey upon oxidation [55]. Similarly, a dansyl substituent pyrrole derivative (**10**) was electropolymerized and a greenish-yellow to greyish-green coloring, green light emitting polymer was achieved[56]. In another inspiring study, electrochemical deposition of a pyrrole-1-yl substituted perylene diimide (**11**) was achieved [57]. Poly(**11**) turned from red (λ_{max} : 573 nm) to emerald (λ_{max} : 788 nm) upon oxidation. For poly(**11**) the time required for reaching 90% of the ultimate absorbance was calculated as 160 s. Such slow response was attributed to the low conductivity of the polymer, which was considered to be due to the large separation of perylene diimide as well as the insulating nature of the polypyrrole backbone in the operating potential range. In 2002 synthesis and electropolymerization of pyrrol-1-yl substituted phthalocyanines was achieved. The resultant displayed charge–discharge behavior which was accompanied by a reversible electrochromic color change [58].

3.2.2. 3- and 3,4-Substituted Polypyrroles

Despite improvements achieved by 3-alkyl substitution of polythiophene derivatives, such as effective bandgap control and color tuning, due to their synthetically demanding nature and their sensitivity to air in the neutral state only a few reports have been published [59-64] on poly(3-alkylpyrrole)s. Some examples include poly(methyl substituted bipyrroles) (poly(**12**)) [65], poly(3-hydroquinonylpyrrole) (poly(**13**)) [66], and poly(3-alkylsulfonate pyrrole)s (poly(**14**)) [67]. Among those, methyl substituted bipyrroles was reported to display transmissive-yellow to gray-blue color transition upon oxidation. Substitution at the 3-position has a less pronounced effect on the oxidation potential and conductivity of the polymer [66]. Compared to N-substituted polypyrroles, these materials were found to be more conductive under optimized conditions (e.g., propylene carbonate as solvent and hexafluophosphate as counter ion).

Besides their important role in modification of electrical and optical properties of the polymers, substitution through 3- and 4-positions of thiophene (as of pyrrole) is expected to prevent the undesirable α-β couplings during polymerization, which are known to decrease effective conjugation length and the solubility of polythiophenes. In general, substitution through 3- and 4-positions allows polymerization to proceed through the 2- and 5-positions which yields a polymer with fewer structural defects.

1990s witnessed the tremendous improvement in electrochromic properties of polythiophene derivatives through the breathtaking growth of poly(3,4-alkylenedioxythiophene) (PXDOT) family. PXDOT derivatives have developed as easily oxidizable, low bandgap materials with good stability [68] . Birth of PXDOT derivatives was achieved by the pioneer work of Jonas et al. [69], who were the first to anodically polymerize EDOT. The resultant cathodically coloring polymer had a bandgap of 1.6 eV and displayed coloration from almost transparent (with a sky-blue tint) to dark blue. PEDOT exhibited a bandgap that is 1.1 eV lower than that of PPy and 0.5 eV lower than that of polythiophene. The decline in the bandgap of the polymer was attributed to the tendency of the oxygen atoms to donate electron density, which results in an increase in highest occupied molecular orbital (HOMO) of the π-system and leads to a decline in the bandgap. Later on, intense studies were devoted to expand the range of substituted 3,4-alkylenedioxy thiophenes, having different ring sizes and substituents. The response time of both PEDOT and 7-membered PProDOT [69,70] was recorded as 2.2s, whereas 8-membered PBuDOT revealed 1.3 s [71]. Moreover, optical contrast (Δ%T) of the polymers increased with the increase in size of the alkylenedioxy ring from 44% for PEDOT to 54% for PProDOT to 63% for PBuDOT. Among those, ProDOT has become the center of attention owing to its facile functionalization at the central carbon of the propylene bridge.



Especially, its dimethyl substituted derivative Me_2PProDOT) showed a highly transmissive doped state with 78% optical contrast and a switching time of 0.3 seconds (reported at 95% of full contrast) [72].

Following the breathtaking growth of PXDOT family, a new class of easily oxidized electroactive conjugated polymer was born through attachment of alkylenedioxy bridge to the 3- and 4-positions of pyrrole, namely poly(3,4-alkylenedioxypyrrole)s (PXDOPs) [73]. The pioneer member, PEDOP revealed a bandgap of 2.0 eV with an optical contrast of 59% [74]. Contrary to its cathodically coloring thiophene analogue (PEDOT), PEDOP displayed red color in neutral state and sky blue-transparent in oxidized state. Below scheme reflects some of the members of this unique family which includes various dialkyl, alkylene, *N*-hydro, and *N*-alkyl derivatives. It was shown that the optoelectronic properties of PXDOPs can be modified by changing the size, the composition of the alkylene bridge and N-substitution (Table 1). Contrary to its thiophene analogs, increasing the ring size from 6-membred to 7- and 8-membred ring in pyrrole derivatives did not gradually increase the optical contrast.

For instance, as in the case of poly[3,4-(propylenedioxy)pyrrole] (PProDOP)), MePProDOP and Me_2PProDOP, functionalization

Table 1 Electrochromic properties of PXDOPs

Monomer	E_g [eV]	Colors		λ_{max} [nm]
EDOP	2.0	red sky blue	(n) (d)	537
ProDOP	2.2	orange brown gray-blue	(n) (i) (d)	522
MeProDOP	2.2	orange red-brown light blue	(n) (i) (d)	530
Me_2ProDOP	2.2	orange red-brown light blue	(n) (i) (d)	534
BuDOP	2.2	orange blue-gray	(n) (d)	533
CrownDOP	2.4	yellow transparent gray	(n) (d)	490
ProDOP-*N*-Me	3.0	deep purple dark green blue	(n) (i) (d)	476
ProDOP-*N*-Gly	3.4	colorless pink tan gray-blue	(n) (i) (i) (d)	460
ProDOP-*N*-PrS	2.9	colorless pink gray blue-gray	(n) (i) (i) (d)	460
PProDOP-N-$C_{18}H_{37}$	2.96	colorless faint pink slightly grey	(n) (i) (d)	350

[a] E_g: optical bandgap (eV) ; λ_{max}: wavelength of maximum absorption.

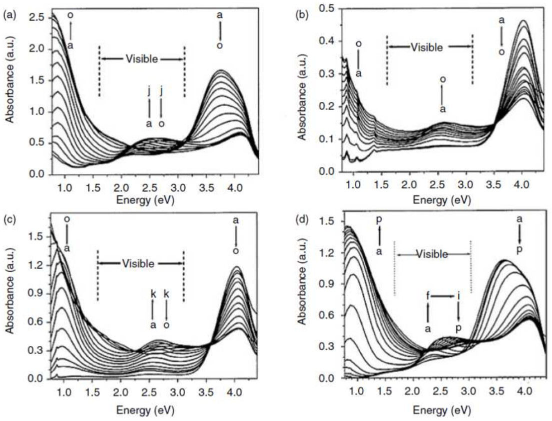


Fig. 7 Absorbance spectroelectrochemistry for thin films of (a) PProDOP-N-Me switched between -0.5 and 0.7 V, (b) PProDOP-N-Pr switched between -0.4 and 0.6 V, (c) PProDOP-N-Gly switched between -0.2 and 0.7 V, and (d) PProDOP-N-PrS switched between -0.4 and 0.5 V [76].

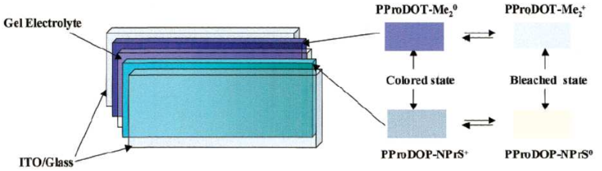


Fig. 8 The general scheme for construction of a dual polymer electrochromic device. ITO: indium tin oxide [77]

of the alkyl bridge resulted in formation of multichromic polymers with bandgaps of 2.2 eV [75].These polymers switched from orange to a red-brown (or orange-brown) and finally to a light blue when fully neutralized, partially oxidized, fully oxidized, respectively. Me_2PProDOP, having optical contrast of 76% (at 534 nm) retained 90% of its electroactivity after undergoing 40,000 potential switches. On the other hand, PProDOP-*N*-Pr revealed higher bandgap compared to its *N*-hydro derivative (PProDOP) due to the distortion of the polymer backbone, giving rise to a decline in the effective conjugation and lowering of the valance band [76]. Moreover, utilization of sterically demanding substituents, as in the case of PProDOP-N-Gly and PProDOP-*N*-PrS, increased the bandgap up to 3.4 eV and lead to full visible light transmissivity in neutral state (Fig 7). In general, N-alkylated PXDOP derivatives are shown to have high bandgap, high conductivity, and low half-wave potential, which made them strong candidates as anodically coloring materials in electrochromic devices. One such example was provided in a 2002 study [77] where a complementary controlled dual type electrochromic device was constructed (Fig 8), having PProDOP-NPrS as the anodically and Me_2PProDOT as the cathodically coloring polymer. It was shown that utilization of PProDOP-NPrS not only provided a transmissivity window throughout the entire visible spectrum but also enhanced optical contrast of the device from 56% to 68% (measured at 580 nm). Moreover, the device was found to retain 86% of its optical response after 20 000 double potential steps. In another study, films of PProDOP was paired with PEDOT and PProDOP in a stacked polymer arrangement to achieve dual-polymer electrochromic films [78]. By coupling of these polymers logically and by keeping each layer under separate potentiostatic control, a wide range of colors was achieved.

Additionally, solution-processable, minimally color-changing dioxypyrrole-based polymer (PProDOP-N-$C_{18}H_{37}$) with high level of electroactivity was achieved [79]. The neutral polymer (E_g=2.96 eV) exhibited its maximum absorption in UV region with an onset at 420 nm and appeared to be colorless (Fig 9). At the intermediate state, the polymer's transparency decreased and it displayed a faint pink hue due to formation of polaron bands centered at around 525 nm. Upon further oxidation, the polymer showed bipolaronic transitions in near infrared region with a very slight grey hue. During repetitive redox cycling, the percent electroactivity of the polymer dropped only 10% in the first 35,000 cycles. Moreover, dual polymer absorptive/transmissive devices were constructed with poly((2,2-bis(2-ethylhexyloxymethyl)-propylene-1,3-dioxy)-3,4-thiophene-2,5-diyl) (ECP-Magenta) and PProDOP-N-$C_{18}H_{37}$, where the latter

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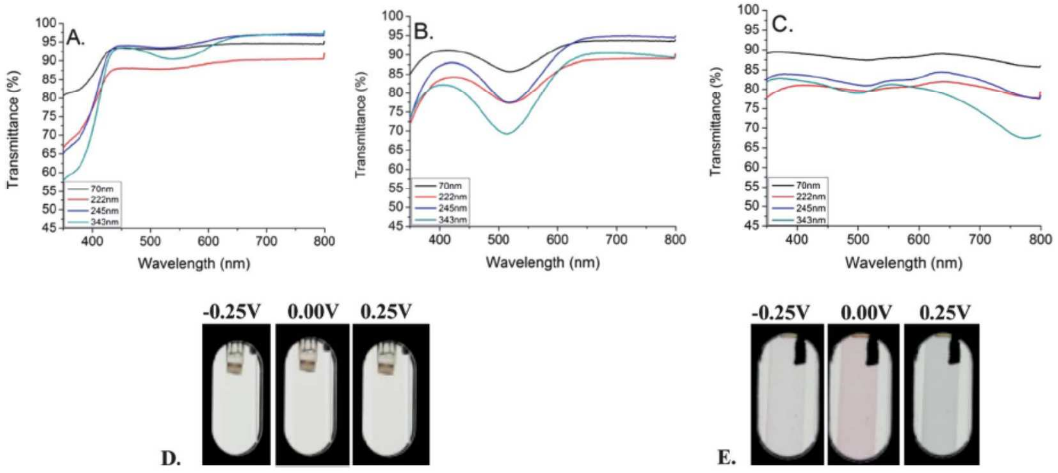
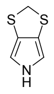


Fig.9 UV/Vis-NIR transmittance spectra for the neutral (A), intermediate (B), and oxidised (C) states of PProDOP-N-$C_{18}H_{37}$) of increasing thickness, spray-cast onto ITO glass. Photographs show the films of 70nm (D) and 343nm (E) thickness at the voltages indicated [79].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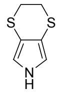
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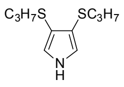
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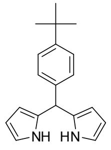
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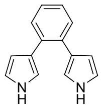
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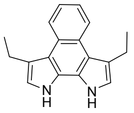
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functioned as the charge balancing, low coloration efficiency, counter electrode. The ability of the polymer to exhibit minimal color change during a switch resulted in high contrast and maximum transmittance of the electrochromic device in the bleached state. Later on, the very same electrochromic polymers were utilized in manufacturing of organic photovoltaic-powered electrochromic displays [80]. Using roll coating methods and printable electrolytes fully printable and laminated devices on flexible substrates were constructed. Devices of various sizes were constructed, having optical contrast of 58% at a visible wavelength of 550 nm and switching times of <10 s. With this pioneer study fabrication of a self-powered OPV/ECD module was established.

To further elucidate the effect of 3,4-disubstitution on polypyrrole derivatives; poly(3,4-methylenedithiopyrrole) (poly(**15**)), poly(3,4-ethylenedithiopyrrole) (poly(**16**)) and poly(3,4-bis(propylthio)pyrrole) (poly(**17**)) were also synthesized [81] whose bandgaps were determined to be 1.8, 2.1 and 2.3 eV, respectively. These bandgaps are lower than PPy and comparable to those of PXDOPs as discussed previously. The relative increase in bandgaps was considered to be due to variation of the biaryl torsional angles that is stimulated by size of the alkylthio substituents. Interestingly, these polymers showed significantly high in situ conductivities that are comparable to PPy. A moderate bandgap polymer (E_g=2.39 eV) was synthesized upon electrochemical polymerization of dipyrromethane derivative (**18**) [82]. The polymer revealed color change from yellow to blue upon oxidation with a switching time of 1.2 s. Upon electrochemical copolymerization of 1**8** with EDOT, a new polymer with lower bandgap (1.7 eV) was achieved [83]. In another study, β-linked dipyrrole monomer (**19**) was developed and polymerized electrochemically [84]. It was proposed that oxidation of the monomer leads to intramolecular cyclization followed by polymerization to give α-α coupled polymer. The polymer displayed yellow to black coloration upon oxidation. Following this study, a new structure (**20**) was particularly designed via annulation of the phenyl ring to offer enforced planarity between the adjacent pyrroles and to provide unequivocal reactivity at the pyrrole α-positions due to blocking of the β-positions by alkyl substituents [85]. This multichromic polymer gone through color variations from pale-yellow, to red, to green, and then to blue upon oxidation (Fig 10). Such behavior was attributed to the formation of neutral, polaron, bipolaron and transverse bipolaron states. The coloration efficiency and switching time of the polymer were calculated as 6-7s and 98 cm^2/C at 700 nm, respectively.

3.2.3. Hybrid Systems

A strategy that has been proven to be useful in controlling the optoelectronic properties of conjugated polymers is to use terarylene monomers which combine two heterocycles (thiophene, pyrrole etc.) with a central aromatic unit. It was shown that utilization of terarylene monomers not only reduces the polymerization potential but also provides an opportunity to tune the optical and redox properties. In that perspective, a series

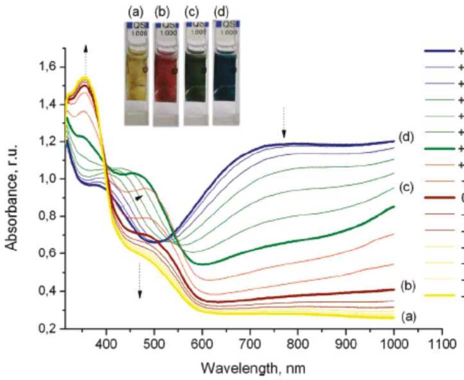
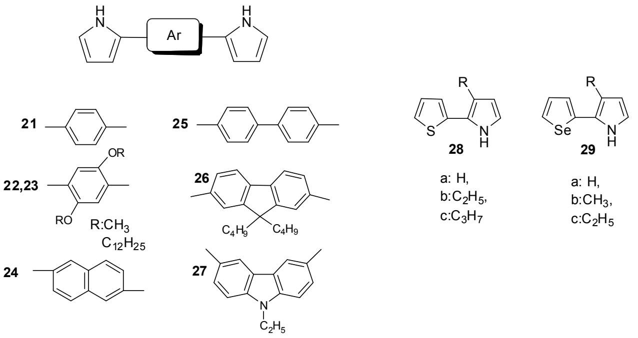


Fig.10 Results of spectroelectrochemical studies of poly(**20**) film deposited on an ITO electrode. Arrows denote changes in the spectra associated with a decrease in the applied potential [85].

of arylene derivatized poly(bis(pyrrol-2-yl) arylene)s, were synthesized through electrochemical polymerization of their respective monomers in 0.1 M tetrabutylammonium perchlorate (TBAP) acetonitrile system [86]. Bandgaps for these polymers (poly(**21**)- poly(**25**)) were found to lay between 2.3 and 2.4 eV, which are lower than that of PPy and poly(*p*-phenylene) (3.0 eV). Lowering of the bandgap was attributed to the increased structural regularity induced by the presence of arylene units. Poly(**21**) and poly (**25**) were stable up to 2300 and 6000 double potential steps before 50% loss of electroactivity, respectively. In another study [87], a fluorene containing polymer was synthesized through electrochemical polymerization of 9,9-diethyl-2,7-bis(pyrrol-2-yl) fluorene (**26**). Spectroelectrochemical analysis of poly(**26**) revealed a bandgap of 2.4 eV which is identical with to bandgap of poly(**21**). In contrast to its analogues, poly(**27**) revealed two high energy π- π* absorption with an E_g of 2.5 eV [88]. However, it was not possible to reduce (neutralize) the polymer by means of electrochemical methods, which is considered to be due to its facile oxidation. Unlike other analogues, poly(**27**) is not fully conjugated since the conjugation is broken at the nitrogen atom of the carbazole, which in turn leads to localization of the charge carriers between consecutive carbazole units. On the other hand, poly(bis-EDOT-N-methylcarbazole) [89] having bandgap of 2.5 eV appeared yellow in neutral state. Upon oxidative doping, the polymer showed two distinct redox processes which led to an additional color state, green at intermediate potentials (radical cation) and blue when fully oxidized (dication). Such multichromic behavior was again considered to be related to formation of `discrete` conjugated units along the polymer backbone owing to the nitrogens of the carbazole unit.

As an alternative approach, Trofimov et al. synthesized a conducting polymer with a repeat unit of 2-(2-thienyl)-1*H*-pyrrole (**28a**) in order to combine the electrochromic properties of polythiophene and PPy [90]. The polymer (poly(**28a**)) displayed orange to black coloration with an optical contrast of 19% (at 450 nm). The polymer had a bandgap of 1.6 eV which is significantly lower than two parent polymers. For the bleaching process coloration efficiency and switching time of the polymer was calculated as 233 cm^2/C and 1.3 s (90% of the total absorbance span), respectively. In order to address the effect of substituents, pyrrole unit was functionalized with ethyl (**28b**) and *n*-propyl (**28c**) substituents and subjected to electrochemical polymerization [91]. The resultant polymers were multichromic and showed five different colors ranging from dark orange, orange-yellowish, brown, blue to blue-grayish. For both polymers, switching time was in the range of a few seconds with a coloration efficiency of 107-108 cm^2/C during the bleaching process. In order to shed light on the interactions between selenophene and pyrrole derivatives, another inspiring study was performed in 2009, where a series of 2-(selenophen-2-yl)pyrrole derivatives were synthesized and electrochemically polymerized [92]. Poly(**29a**) revealed λ_{max} at 445 nm and it displayed color variation from orange to black upon oxidation as in the case of its thiophene analogue poly(**28a**). On the other hand poly(**29b**) (λ_{max}=488 nm) and poly(**29c**) (λ_{max}=459 nm) displayed deep-orange and greyish-blue at their extreme states. The optical contrasts of these polymers were in the range of 13 and 26% in the visible region.



In recent years an exciting class of conducting polymer, poly(2,5-dithienyl-1-substituted-pyrrole) (PSNS) poly**(30)** derivatives have been thoroughly investigated for their electrochromic properties [93-126]. Due to their terarylenic structures, all the monomers and their corresponding polymers (Fig 11) exhibited low oxidation potentials. In general all homopolymers (E_g= 1.9 to 3.1 eV) displayed yellow to blue coloration with switching times of 1.3 – 2 s. On the other hand, polymers synthesized through chemical polymerization of benzyl [105], phenyl [104], 4-fluorophenyl [96], petafluorophenyl [95], 4-nitrophenyl [97], benzenamine [98] substituted derivatives were soluble in common organic solvents. In a recent study clickable, azide containing polymers based on 1-(2-azido-ethyl)-2,5-dithiophene-2-yl-1H-pyrrole (SNS-N_3) were synthesized. This polymer was shown to offer multipurpose platform for simple, effective post-functionalization of PSNS under mild conditions [93]. Later on, both p- and n-dopable naphthalimide containing PSNS derivative was synthesized [120]. Other than chemical tailoring through the pyrrole unit, coloring tuning in PSNS derivatives was also accomplished via copolymerization. Copolymers of some of the PSNS derivatives with EDOT revealed an impressive set of multichromic polymers with enhanced electrochromic properties. For instance, the copolymer synthesized through potentiodynamic electrolysis of 1-benzyl-2, 5-di(thiophen-2-yl)-1H-pyrrole and EDOT revealed enhanced optic contrast, switching time compared to parent polymer and multichromism throughout the entire visible region, displaying

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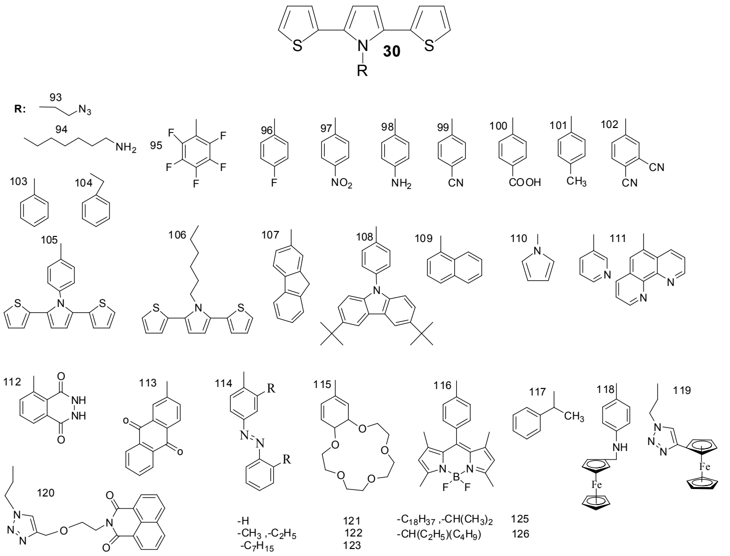


Fig.11 Schematic representation of 2,5-dithienyl-1-substituted-pyrrole derivatives available in literature. (Given numbers relates the structures with the relevant articles)

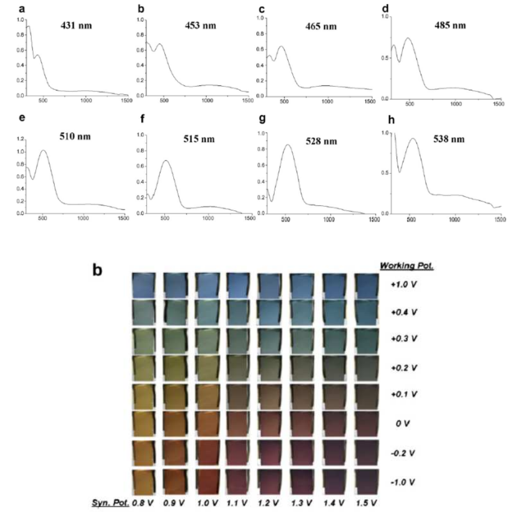


Fig.12 Optical spectra of and copolymers of 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzenamine and EDOT applied potentials (a) 0.8, (b) 0.9, (c) 1.0, (d) 1.1, (e) 1.2, (f) 1.3, (g) 1.4, and (h) 1.5 V [98].

claret red, yellow, green, and blue colors upon variation of the applied potential [127]. Towards multicolored electrochromic polymers, selectivity of the electrochemical polymerization was utilized to synthesize compositionally different copolymers of 4-(2,5-di(thiophen-2-yl)-1H-pyrrol-1-yl)benzenamine and EDOT by varying the applied potential at a constant monomer feed ratio. Fig 12a represents the absorption spectrum of eight different copolymers (in neutral state) which were synthesized at eight different potentials. As seen, there is progressive increase in wavelength of maximum absorption between 431 to 538 nm which the increase in polymerization potential. Fig 12 b reflects colors of these polymers at various oxidation states [98]. In a later recent study, 16 different ambipolar, multichromic naphthalimide containing copolymers were synthesized by controlling electrochemical copolymerization conditions such as feed ratio, electrochemical polymerization method and potential [120]. Fig 13 represents the colorimetry studies of the polymers which were synthesized during potentiodynamic cycling.

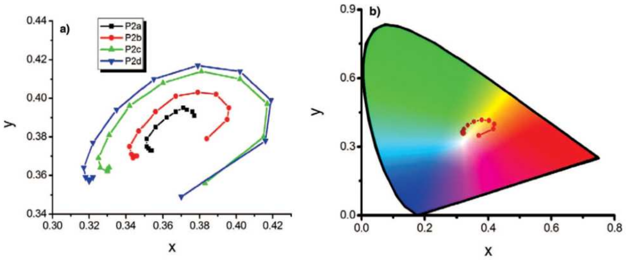
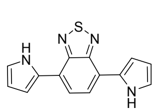


Fig.13. a) x,y data of P2 type polymers, b) representation of chromaticity data of P2d on "horse shoe" diagram (Copolymers synthesized via potentiodynamic scanning from 0.0 V to 1.0 V, to 1.1 V, to 1.2 V, to 1.3 V in EDOT rich media are abbreviated as P2a, P2b, P2c, P2d respectively) [120].

3.2.4. Donor-Acceptor Approach

Another ground breaking approach that has been frequently used to control the bandgap and to tune the colors of the conducting polymers is to synthesize polymers that enclose electron-withdrawing (A) and electron-donating (D) moieties in an alternating, conjugated manner. Through this approach it is expected to increase double bond character between repeating units due to the mesomerism ($D\text{-}A \rightarrow D^{+}=A^{-}$). Effective control of optoelectronic properties is possible through judicious selection of D-A units taking into account their strengths and extent of conjugation [128,129]. Although thiophene derivatives have been extensively used in these systems, in recent years there is a growing interest in utilization of pyrrole as the donor unit.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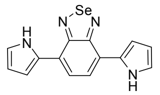
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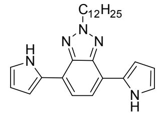
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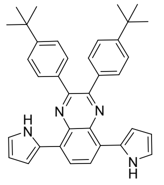
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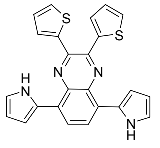
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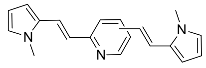
a: 2,6-pyridine derivative
b:2,5-pyridine derivative
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An interesting class of acceptor group is benzazole derivatives which are known for their high electron accepting ability through the two electron-withdrawing imine nitrogen atoms. Due to the differences in chemical properties between nitrogen, sulfur and selenium atoms, pyrrole polymers containing benzothiadiazole (**31**), benzoselenadiazole (**32**) and benzotriazole (**33**) were synthesized [130, 131]. Poly(**31**), poly(**32**) and poly(**33**) exhibited bandgap of 1.12, 1.08 and 1.6 eV respectively. Poly(**31**), poly(**32**) switched from green to blue at around 1s with an approximate optical contrast of 35% [130] . On the other hand poly(**33**) displayed color transition from blue to light blue upon oxidative doping [131]. Due to outstanding electron withdrawing capacity of benzothiadiazole unit, this polymer was n-type dopable with a light blue appearance. On the other hand, the polymer which incorporates pyrrole with tert-butylphenyl substituted quinoxaline (poly(**34**) exhibited two distinct absorption maxima (Fig 14) due to high energy (λ_{max}= 408 nm) and low energy (λ_{max}= 745 nm) π–π * transitions [132]. Color of the polymer changed from saturated green to brownish green at 0.6 s (measured at 408 nm) with a coloration efficiency of 85 cm^2/C. In order to enhance the electrochromic properties of copolymer of (**34**) with bis(3,4-ethylenedioxythiophene), (BiEDOT) was synthesized [133]. The polymer revealed multicolor electrochromic properties with distinct colors (purple, gray, light green, blue), reasonable switching time (1.2s) and optical contrast (23 %) in the visible range. Another polymer of pyrrole with 2,3-di(thiophen-2-yl)quinoxaline (poly(**35**) exhibited a bandgap of 1.0 eV and a green to gray coloration upon doping [134]. The polymer possessed 66% optical contrast in the near IR region with a switching time of 1.2 s. Subsequently, the copolymer of (**35**) with BiEDOT was synthesized [135]. The resulting polymer had a λ_{max} at 525 nm (E_g=1.4 eV) with a purple color in neutral state. The copolymer achieved 10% optical contrast around 2 s in the visible range. Despite their low bandgaps (1.5 eV) vinylene-linked donor–acceptor polypyrroles (poly (**36**)), revealed modest optical contrast [136].

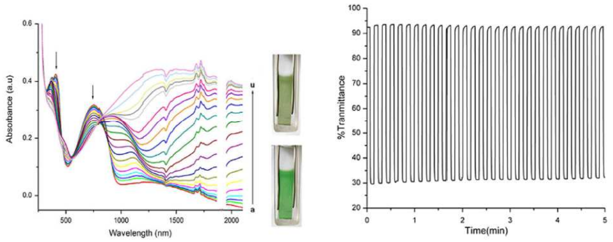

Fig. 14 Spectroelectrochemistry and electrochromic switching poly(**31**) film on ITO-coated glass slide [113].

4. Conclusion and outlook

Among many electrochromic materials, conducting polymers have been the center of interest due to their good mechanical properties, non-dependence to angle of vision, effective tuning of the color through tailoring of polymer's chemical structure, high coloration efficiency and short switching times. For some time, synthetic challenges of pyrrole chemistry limited the progress of polypyrroles when compared with polythiophenes. However, with the recent synthetic advances, the polymers with building blocks of pyrrole derivatives have matured into an extensive family, having low oxidation potential, relative stability and conductivity. Extensive studies on modification of polypyrrole's structure through N-substitution, 3,4-substitution and utilization of donor acceptor approach paved the way for the control of critical issues. Especially, utilization and modification of alkylenedioxypyrrole building blocks afforded a new family of anodically coloring polymers with low oxidation potential.

Unfortunately, despite the presence of a vast variety of electrochromic polymers (especially, for polythiophene derivatives) not much of them are of practical utility. This is mainly due to unresolved technical issues of electrochemical polymerization (which is probably not the best technique for commercialization) or absence of stable polymers which are compatible with the nowadays printing techniques such as ink-jet printing or roll to roll processes. Further efforts should now be headed toward designing polymers that are solution-processable, having at least one accessible highly transmissive state with long-term environmental stability. Very recently, stability of conducting polymer films was improved by employing barrier foils capable of protecting the films from atmospheric oxygen and/or UV irradiation [137]. Despite the compromise in optical contrast and switching ability of the polymers, application of barriers drastically lowered the photochemical decomposition rate of the polymer films. Especially for large-area devices the issues such as long response time, poor stability and high cost might be overcome through utilization of nanostructures [138]. Having large specific surface areas, ultrathin nanowires or nanotubes are expected to reveal fast and stable electrochromic response. One such study was conducted with PEDOT nanotubes where responses of less than 10 ms was achieved due to presence of short diffusion distances as 10–20 nm [139]. Despite its low optic contrast, this case study underlined the importance of structural control for achieving the requirements of display technologies. Additionally, issues on electrode-polymer interactions, electrode adhesion, electrolyte-polymer interactions, formulation of robust manufacturing processes and methodologies of effective encapsulation are yet to be addressed. Utilization of gallium doped ZnO (GZO), antimony doped tin oxide (ATO), PEDOT:PSS, carbon nanotubes or graphene coated glass were shown to provide liable alternatives of the typical optically transparent electrode, ITO. Due to its high bending radius, chemical inertness, large surface area and low surface resistivity single-walled carbon nanotube (SWCNT) films have recently become a featured candidate [140]. Unfortunately, not having coordinative interactions and hydrogen bonding, some of the devices constructed with SWCNT were shown to suffer from long term delamination for which the issue was later resolved through tailoring of polymer's structure [141]. Moreover, to improve the mass transport and to compensate the adverse effect of volume change during electrochemical switching (which causes deterioration of the adhesion between the polymer film and electrode) utilization of nano-structured electrodes should be considered. Continuing the research especially on stability, electrode-polymer interactions would further enhance development of the field. With that being done, polymer electrochromics will be in our daily life as displays, e-papers, rear-view mirrors, smart windows etc. which are only limited by the imagination of researchers.

Notes and references

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1 R.J. Mortimer, A.L. Dyer and J.R. Reynolds, *Displays*, 2006, **27**, 2.
2 R.J. Mortimer, *Chem. Soc. Rev.,* 1997, **26**, 147.
3 S.K. Deb, *Appl. Opt. Suppl.,* 1969, **3**, 192.
4 D.T. Gillaspie, R.C. Tenent and A.C. Dillon, *J. Mater. Chem*., 2010, **20**, 9585.
5 C.G. Granqvist, *Solar En.Mater. Solar Cells,* 2000, **60**, 201.
6 C.L. Bird and A.T. Kuhn, *Chem. Soc. Rev.,* 1981, **10**, 49.
7 R. J. Mortimer, *Electrochim. Acta*, 1999, **44**, 2971.
8 A. L. Dyer and J. R. Reynolds: Electrochromism of Conjugated Conducting Polymers in T.A. Skotheim and J.R. Reynolds (eds.) Handbook of Conducting Polymers Third Edition Conjugated polymers theory, synthesis, properties, and characterization, CRC Press Taylor & Francis Group 2007.
9 Çamurlu, P. and Toppare L.: Electrochromism in Conducting Polymers. In: Somani P.R. (ed.) Chromic Materials, Phenomena and Their Technological Applications, Applied Science Innovations Private Ltd. Maharasthra (2010).
10 P. Monk, R. Mortimer and D. Rosseinsky, Electrochromism and Electrochromic Devices Cambridge University Press, Cambridge (2007).
11 V. K. Thakur , G. Ding , J. Ma , P. S. Lee and X. Lu, *Adv. Mater.,* 2012, **24**, 4071.
12 A.A. Argun, P.-H. Aubert, B. C. Thompson, I. Schwendeman, C. L. Gaupp, J. Hwang, N. J. Pinto, D. B. Tanner, A. G. MacDiarmid and J. R. Reynolds, *Chem. Mater.,* 2004, **16**, 4401.
13 D.S. Dalavi, R. S. Devan, R. A. Patil, R. S. Patil,Y-R. Ma, S. B. Sadale, I.Y. Kim, J-H. Kim and P. S. Patil, *J. Mater. Chem. C,* 2013, **1**, 3722.
14 C.K. Chiang, C.R. Fincher, Y.W. Park, A.J. Heeger, H. Shirakawa, F.J. Louis, S.C. Gau and A.G. MacDiarmid, *Phys. Rev. Lett.*, 1977, **39**, 1098.
15 L.-X. Wang, X.-G. Li and Y.-L. Yang, *React. Func. Polym.*, 2001, **47**, 125.
16 L.B. Groenendaal, G. Zotti,P. H. Aubert, S.M. Waybright and J. R. Reynolds, *Adv. Mater.,* 2003, **15**, 855.
17 B.L. Funt and A.F. Diaz, Organic Electrochemistry: an Introduction and a Guide, Marcel Dekker, New York, 1991, 1337.
18 E. M. Genies, G. Bidan and A. F. Diaz, *J. Electroanal. Chem.,* 1983, **149**, 101.
19 R.J. Waltman and J. Bargon, *Can. J. Chem.,* 1985, **64**, 76.
20 R.J. Waltman and J. Bargon, *Tetrahedron*, 1984, **40**, 3963.
21 S. Sadki, P. Schottland, N. Brodie and G. Sabouraud, *Chem. Soc. Rev.*, 2000, **29**, 283.
22 J. Roncali, *Chem. Rev.* 1992, **92**, 711.
23 M. Zhou and J. Heinze *J. Phys. Chem. B,* 1999, **103**, 8443.
24 S.H. Cho, K. T. Song, and J. Y. Lee Recent Advances in Polypyrrole in T.A. Skotheim and J.R. Reynolds (eds.) Handbook of Conducting Polymers Third Edition Conjugated polymers theory, synthesis, properties,and characterization, CRC Press Taylor & Francis Group 2007.
25 J.L. Bredas and G.B. Street, *Acc. Chem. Res.*, 1985, **18**, 309.
26 A.O. Patil, A.J. Heeger and F. Wudl, *Chem. Rev.*, 1988, **88**, 183.
27 K. Yakushi, L.J. Lauchlan, T.C. Clarke, and G.B. Street, *J. Chem. Phys*., 1983, **79**, 4774.
28 S. Panero, , S. Passerini and B. Scrosati, *Mol. Cryst. Liq Cryst.*, 1993, **229**, 97.
29 J. Roncali, *Chem. Rev.,* 1997, **97**, 173.
30 P.R. Somani and S. Radhakrishnan, *Mater. Chem. Phys.,* 2002, **77**, 117.
31 E.M. Girotto and M.A. De Paoli, *Adv. Mater*., 1998, **10**, 790.
32 J. Ferreira , M.J.L. Santos , R. Matos , O.P. Ferreira , A.F. Rubira and E.M. Girotto, *J. Electroanal. Chem*., 2006, **591**, 27.
33 F. Tavoli and N. Alizadeh, *J. Electroanal. Chem*., 2014, **720–721** 128.
34 Yamada, K. Seya and G. Kimura, *Synth. Met,*. 2009, **159**, 188.
35 Shimidzu, T., A. Ohtani, M. Aiba, and K. Honda, *J. Chem. Soc. Faraday Trans. 1*, 1988, **84**, 3941.
36 A.C. Sonavane, A.I. Inamda, D.S. Dalavi, H.P. Deshmukh and P.S. Patil, *Electrochim. Acta*, 2010, **55**, 2344.
37 S. Takagi, S. Makuta, A. Veamatahau, Y. Otsuka and Y. Tachibana, *J. Mater. Chem*., 2012, **22**, 22181.
38 M. Shibata, K.-I. Kawashita, R. Yosomiya, H. An and Y. Haga, *J. Macromol. Sci., Part A,* 1998, **35**, 1207.
39 R. Brooke, D. Evans , P. Hojati-Talemi, P. Murphy and M. Fabretto *Eur. Polym. J.,* 2014, **51**, 28.
40 S. Ahmad and S. Singh, *Electrochem. Commun*. 2008, **10**, 895.
41 I.D. Brotherstona, D.S.K. Mudigondaa, J.M. Osborna, J. Belka, J. Chena, D.C. Lovedaya, J.L. Boehmea, J.P. Ferrarisa and D.L. Meeker, *Electrochim. Acta,* 1999, **44**, 2993.
42 M. Ak, B. Gacal, B. Kiskan, Y. Yagci and L. Toppare, *Polymer*, 2008, **49**, 2202.
43 Z. Zhao-yang, T. Yi-jie, X. Xiao-qian, Z. Yong-jiang, C. Hai-feng and Z. Wen-wei, *J. Appl. Polym. Sci.* 2013, **129**, 1506.
44 T. Yi-jie, C. Hai-feng, Z. Wen-wei, Z. Zhao-yang and L. Dong-qing, *Synth. Met*, 2012, **162**, 728.
45 T.C. Wen, C.H. Yang, Y.C. Chen, and W.C. Lin, *J.Electrochem. Soc*., 2003, **150**, D123.
46 A.F. Diaz, J. Castillo, K.K. Kanazawa and J.A. Logan, *J. Electroanal. Chem.,* 1982, **133**, 233.
47 Y. Murakami and T. Yamamoto, *Polym. J.,* 1999, **31**, 476.
48 W.A. Gazotti, M.-A. De Paoli, G. Casalbore-Miceli, A. Geri, and G. Zotti, *J. Appl. Electrochem*., 1999, **29**, 753.
49 M.-A. De Paoli, , G. Casalbore-Miceli, E.M. Girotto, and W.A. Gazotti, *Electrochim. Acta,* 1999, **44**, 2983
50 M. Ak, M.S. Ak and L. Toppare, *Macromol. Chem. Phys.,* 2006, **207**, 1351.
51 P. Camurlu and C. Gültekin, *Smart Mater.Struct.*, 2012, **21**, 025019.
52 P. Camurlu, E. Eren and C. Gültekin, *J. Polym. Sci. Part A*, 2012, **50**, 4847.
53 O. Mert, A. S. Demir and A. Cihaner, *RSC Advances*, 2013, **3**, 2035.
54 M. Ouyang, G. Wang and C. Zhang, *Electrochim. Acta,* 2011, **56**, 4645.
55 E. C.S. Coelho, V. B. Nascimento, A. S. Ribeiro and M. Navarro, *Electrochim. Acta*, 2014, **123**, 441

56 A. K.A. Almeida, J. M.M. Dias, A. J. C. Silva , D. P. Santos, M. Navarro, J. Tonholo, M. O.F. Goulart and A. S. Ribeiro, *Electrochim. Acta* 2014, **122**, 50.

57 W. Choi, H. C. Ko, B. Moon, and H. Lee, *J.Electrochem. Soc*., 2004, **151,** E80-E83.

58 N. Trombach, O. Hild, D. Schlettwein and D. Wöhrle *J. Mater. Chem.*, 2002, **12**, 879.

59 H. Masuda, S. Tanaka and K. Kaeriyama, *J. Chem. Soc., Chem. Commun*., 1989, 725.

60 K. Kaeiyama, M. Sato and K. Hamada, *Makromol. Chem. Rapid Commun.,* 1989, 171.

61 D.Delabouglise, J. Roncali, M. Lemaire and F. Garnier, *J. Chem. Soc., Chem. Commun.,* 1989, 475.

62 K. Kaeriyama, S. Tanaka, M.-A. Sato and K. Hamada, *Synth.Met.,* 1989, **28**, C611.

63 M. Salmon, A.F.Diaz, A.J. Logan, M. Krounbi and B.Bargon, *J.Mol. Cryst. Liq. Cryst.,* 1982, **83**, 265.

64 T. Jarosz, A. Brzeczek, K. Walczak, M. Lapkowski and W. Domagala, *Electrochim. Acta,* 2014, **137**, 595.

65 T. Benincori, E. Brenna and F. Sannicolo, *Chem. Mater.*, 2000, **12**, 1480.

66 A.B. Kon, J.S. Foos and T.L. Rose, *Chem. Mater.*, 1992, **4**, 416.

67 E.E. Havinga, W. ten Hoeve, E.W. Meijer and H. Wynberg, *Chem. Mater.*, 1989, **1**, 650.

68 F. Jonas, and L. Schrader, *Synth. Me.,*. 1991, **831**, 41.

69 D. M. Welsh, A. Kumar, E. W. Meijer, and J. R. Reynolds, *Adv. Mater*., 1999, **11,** 1379.

70 D. M. Welsh, A. Kumar, M. C. Morvant, and J. R. Reynolds, *Synth. Met*., 1999**, 102**, 967.

71 A. Kumar, D. M. Welsh, M. C. Morvant, F. Piroux, K. A. Abboud, and J. R. Reynolds, *Chem. Mater*., 1998, **10**, 896.

72 C. L. Gaupp, D. M. Welsh, R. D. Rauh, and J. R. Reynolds, *Chem. Mater*., 2002, **14,** 3964.

73 R.M. Walczak and J.R. Reynolds, *Adv. Mater.,* 2006, **18**, 1121.

74 C.L. Gaupp, K. Zong, P. Schottland, B.C. Thompson, C.A. Thomas and J.R. Reynolds, *Macromolecules,* 2000, **33**, 1132.

75 P. Schottland, K. Zong, C.L. Gaupp, B.L. Thompson, C.A. Thomas,I. Giurgiu, R. Hickman, K.A. Abboud and J.R. Reynolds, *Macromolecules,* 2000, **33**, 7051.

76 G. Sonmez, I. Schwendeman, P. Schottland, K.W. Zong and J.R. Reynolds, *Macromolecules,* 2003, **36**, 639.

77 I. Schwendeman, R. Hickman, G. Sonmez, P. Schottland, K. Zong, D. M. Welsh and J. R. Reynolds, *Chem. Mater.,* 2002, **14**, 3118.

78 E. Unur, J-H. Jung, R.J. Mortimer and J.R. Reynolds, *Chem. Mater.,* 2008, **20**, 2328.

79 E.P. Knott, M. R. Craig, D. Y. Liu, J. E. Babiarz, A. L. Dyer and J.R. Reynolds, *J. Mater. Chem.,* 2012, **22**, 4953

80 J. Jensen, H. F. Dam and J. R. Reynolds, A. L. Dyer and F. C. Krebs, *J. Polym. Sci. B*, 2012, **50**, 536.

81 H. Li, C. Lambert and R. Stahl, *Macromolecules,* 2006, **39**, 2049.

82 M. Ak , V. Gancheva , L.Terlemezyan , C.Tanyeli and L Toppare, *Eur. Polym. J.*, 2008, **44**, 2567.

83 M. Ak, H. Cetişli and L Toppare, *Colloid. Polym. Sci.*, 2013, **291**, 767.

84 J. M. Nadeau and T. M. Swager, *Tetrahedron*, 2004, **60**, 7141.

85 V.V. Roznyatovskiy, N.V. Roznyatovskaya, H. Weyrauch, K. Pinkwart, J.Tübke, and J. L. Sessler, *J. Org. Chem.* 2010, **75**, 8355.

86 G.A. Sotzing and J.R. Reynolds, A. R. Katritzky, J. Soloducho,S. Belyakov and R. Musgrave, *Macromolecules*, 1996, **29**, 1679.

87 B. Tsuie, J.L. Reddinger, G.A. Sotzing, J. Soloducho, A.R. Katritzky and J.R. Reynolds, *J. Mater. Chem.,* 1999, **9**, 2189.

88 G.A Sotzing, J.L. Reddinger, A.R. Katritzky, J. Soloducho, R. Musgrave, J.R. Reynolds and P.J. Steel, *Chem. Mater.*, 1997, **9**,1578.

89 J. L. Reddinger, G. A. Sotzing and J. R. *Reynolds, Chem. Commun.,* 1996, 1777.

90 C. Pozo-Gonzalo , J.A. Pomposo, J.A. Alduncin , M. Salsamendi, A.I. Mikhaleva , L.B. Krivdin and B.A. Trofimov, *Electrochim. Acta,* 2007, **52**, 4784.

91 C. Pozo-Gonzalo, M. Salsamendi, J. A. Pomposo,H.J. Grande, E. Y. Schmidt, Y.Y. Rusakov and B.A. Trofimov, *Macromolecules,* 2008, **41**, 6886.

92 B.A. Trofimov, E.Y. Schmidt, A.I. Mikhaleva, C. Pozo-Gonzalo, J.A. Pomposo, M. Salsamendi, N.I. Protzuk, N.V. Zorina, A.V. Afonin, A.V. Vashchenko, E.P. Levanova, and G. G. Levkovskaya, *Chem. Eur. J.,* 2009, **15**, 6435.

93 P. Camurlu and N. Karagoren, *React.Func. Polym*., 2013, **73**, 847.

94 S. Tarkuc, M. Ak, E. Onurhan and L. Toppare, *J. Macromol. Sci., Part A,* 2008, **45**, 164.

95 E. Sahin, E. Sahmetlioglu, I.M. Akhmedov, C. Tanyeli and L. Toppare, *Org. Electron.,* 2006, **7**, 351.

96 A. Arslan, O. Turkaslan, C. Tanyeli, I.M. Akhmedov and L. Toppare, *Mat. Chem. and Phys.*, 2007, **104**, 410.

97 S. Varis, M. Ak, C. Tanyeli, I.M. Akhmedov and L. Toppare, *Eur. Polym. J.*, 2006, **42**, 2352.

98 E. Yildiz, P. Camurlu, C. Tanyeli, I.M. Akhmedov and L. Toppare, *J. Electroanal. Chem.*, 2008, **612**, 247.

99 Y.H. Kim, J. Hwang, J.I. Son and Y. Shim, *Synth. Met.,* 2010, **160**, 413.

100 N.A. Lengkeek, J.M. Harrowfield and G.A. Koutsantonis, *Synth. Met*., 2010, **160**, 72.

101 B.Yigitsoy, S.Varis, C.Tanyeli, I.M. Akhmedov and L. Toppare, *Thin Solid Films*, 2007, **515**, 3898.

102 A. Yavuz, B. Bezgin, L. Aras, A.M. Onal, *J. Electroanal. Chem.*, 2010, **639**, 116.

103 S. Tarkuc, E. Sahmetlioglu, C. Tanyeli, I.M. Akhmedov and L. Toppare, *Electrochim. Acta*, 2006, **51**, 5412.

104 S. Tarkuc, E. Sahmetlioglu, C. Tanyeli, I.M. Akhmedov and L. Toppare, *Sensor Actuat. B-Chem*, 2007, **121**, 622.

105 S. Kiralp, P. Camurlu, G. Gunbas, C. Tanyeli, I.M. Akhmedov, L. Toppare, *J. Appl. Polym. Sci*., 2009, **112**, 1082.

106 M. Ak, E. Sahmetlioglu and L. Toppare, *J. Electroanal. Chem.*, 2008, **621**, 55.

107 A. Cihaner and F. Algı, *Electrochim. Acta*, 2008, **53**, 2574.

108 S. Koyuncu, C. Zafer, E. Sefer, F.B. Koyuncu, S. Demic, I. Kaya, E. Ozdemir and S. Icli, *Synth. Met*., 2009, **159**, 2013.

109 A. Cihaner and F. Algı, *J. Electroanal. Chem.*, 2008, **614**, 101.

110 A. Cihaner, O. Mert and A.S. Demir, *Electrochim. Acta*, 2009, **54**,1333.

111 J. Hwang, I.J. Son and Y. Shim, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 1286.

112 D. Asil, A. Cihaner, F. Algı and A.M. Önal, *Electroanal.*, 2010, **22**, 1.

113 G. Wang, X. Fu, J. Huang, L. Wu and Q. Du, *Electrochim. Acta*, 2010, **55**, 6933.

114 A. Cihaner, F. Algı, *Electrochim. Acta*, 2009, **54**, 1702.

115 F. Algı and A. Cihaner, *Tetrahedron Letters*, 2008, **49**, 3530.

116 A. Cihaner and F. Algı, *Electrochim. Acta*, 2008, **54**, 786.

117 U.H. Yıldız, E. Sahin, I.M. Akhmedov, C. Tanyeli and L. Toppare, *J.Polym. Sci.Part A*, 2006, **44**, 2215.

118 P. Camurlu, Z. Bicil, C. Gültekin and N. Karagoren, *Electrochim. Acta*, 2012, **63**, 245.

119 Z. Bicil, P. Camurlu, B. Yucel and B. Becer, *J. Polym. Research*, 2013, **20**, 228.

120 P. Camurlu and N. Karagoren, *J. Electrochem. Soc.,* 2013, **160**, H560.

121 G.G. McLeod, G.B. Mahboubian-Jones, R.A. Pethrick, S.D. Watson, N.D. Truong, J.C. Galin and J. Francois, *Polymer*, 1986, **27**, 455.

122 A. Berlin, W. Wernet and G. Wegner, *Macromol. Chem. and Phys.*, 1987, **188**, 2963.

123 J.P. Ferraris, R.G. Andrus and D. Hrncir, *J. Chem. Soc., Chem. Commun.,* 1989, **18**, 1318.

124 J.P. Ferraris and T.R. Hanlon, *Polyme*r, 1989, **30**,1319.

125 P. Camurlu, C. Gültekin and Z. Bicil, *Electrochim. Acta*, 2012, **61**, 50.

126 B. C. Thompson, K. A. Abboud, J. R. Reynolds, K. Nakatani and P. Audeber, *New J. Chem.*, 2005, **29**, 1128.

127 P.Camurlu, S. Tarkuc, E. Sahmetlioglu, I. M. Akhmedov, C. Tanyeli, and L. Toppare, *Sol. Energy Mater. Sol. Cells,* 2008, **92**, 154.

128 C. A. Thomas, K. Zong, K. A. Abboud, P. J. Steel, and J. R. Reynolds, *J. Am. Chem. Soc.,* 2004, **126**, 16440.

129 P.M. Beaujuge and J.R. Reynolds, *Chem. Rev.,* 2010, **110**, 268.

130 D. Baran, G. Oktem, S.Celebi and L. Toppare, *Macromol. Chem. Phys*. 2011, **212**, 799.

131 D. Baran, A. Balan, B.M. Esteban, H. Neugebauer, N. S. Sariciftci and L. Toppare, *Macromol. Chem. Phys*., 2010, **211**, 2602.

132 S. Celebi, A. Balan, B. Epik, D. Baran and L. Toppare, *Org. Electron.,* 2009, **10**, 631

133 S.Celebi, D. Baran, A. Balan and L. Toppare, *Electrochim. Acta*, 2010 , **55**, 2373.

134 A.T. Taskin, A. Balan, B. Epik, E.Yildiz, Y. A. Udum and L. Toppare, *Electrochim. Acta*, 2009, **54**, 5449.

135 A. T. Taskin, A. Balan, Y. A.Udum and L. Toppare, *Smart Mater. Struct.,* 2010, **19**, 065005.

136 A. Abbotto, E. H. Calderon, N. Manfredi, C. M. Mari, C. Marinzi and R. Ruffo, S*ynth. Met.,* 2011, **161**, 763

137 J. Jensen, M. V. Madsen and F. C. Krebs, *J. Mater. Chem. C*, 2013, **1**,4826.

138 J. Wang , X. W. Sun , Z. Jiao *Materials*, 2010, 3, 5029-5053

139 C.I Cho, W.J. Kwon, S.-J. Choi, P. Kim, S.-A. Park, J. Kim, S.J. Son, R. Xiao, S.-H. Kim and S.B. Lee, *Adv. Mater*. 2005, **17**, 171.

140 M. Nikolou, A. L. Dyer, T. T. Steckler, E. P. Donoghue, Z. Wu, N. C. Heston, A. G. Rinzler, D. B. Tanner, and J. Reynolds, *Chem. Mater*. 2009, **21**, 5539.

141 S. V. Vasilyeva, E. Unur, R. M. Walczak, E. P. Donoghue,A. G. Rinzler, and J. R. Reynolds, *ACS Appl. Mater. Interfaces*, 2009, **1**, 2288.