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Recent advances in triphenylamine-based electrochromic derivatives and polymers

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Triphenylamine-containing electrochromic materials revealing significant color changes by electrochemically induced redox reactions are attractive with great potential for low energy-consumption displays, light-adapting mirrors in vehicles, and smart window applications. These materials have experienced an exponential growth of research interests and have rapidly developed into an emerging field. In this review, the newly developed triphenylamine-based derivatives and polymers in the past few years are summarized, with emphasis on the synthetic approaches as well as their potential applications.

1. Introduction

The propeller-shaped triphenylamine (TPA) has become a promising optoelectronic molecule for emergent electronic applications owing to the prerequisites of its good thermal and morphological stability.[1–8] To date, a huge number of TPA-based electrochromic (EC) materials have been explored and suggested for use in practical applications.[9–12] They have a

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broad range of material systems, including high-performance polymers (aromatic polyimides or polyamides), conjugated polymers, epoxy resins, polysiloxane gels, metal complexes, and small molecules and nearly all these EC materials revealed specific and interesting EC behaviors.

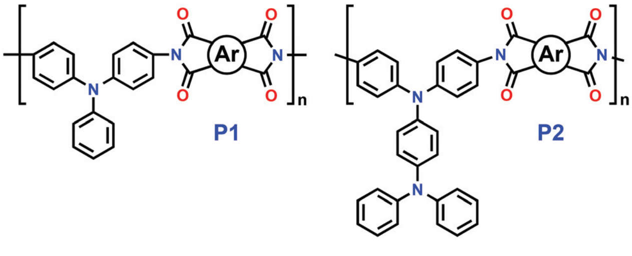
Although TPA-based EC materials have been extensively studied for more than one decade, there is still no other comprehensive review since 2012.[13] Thus, we try to highlight the latest advancements of different EC systems with the perspectives and future opportunities in this review, and focus on the structural design concepts, basic electrochemical behaviors and EC performances.

2. Triphenylamine-based polyimides

Among the high-performance polymers,[14–26] aromatic polyimides (PIs) can be categorized as an important class of materials because of their outstanding and desirable characteristics. In addition, aromatic PIs can be considered as an alternative to glass and metals in many industrial applications, especially in the semiconductor and electric packaging industry. The charge transfer (CT) complex formation could be attributed to the strong intramolecular and intermolecular interactions between electron-donating (diamine moiety) and electron-accepting (dianhydride moiety) segments. TPA-based PIs **P1** were first prepared in 1991 from 4,4′-diaminoTPA and various tetracarboxylic dianhydrides (Scheme 1).[27–29] These thermally stable PIs were mostly soluble in many polar solvents associated with high glass-transition temperatures (T_g) and high char yields.

In 2005, our group prepared the first EC aromatic PIs **P2** with pendent TPA units from the newly synthesized diamine, *N*,*N*-bis(4-aminophenyl)-*N*′,*N*′-diphenyl-1,4-phenylenediamine, and various tetracarboxylic dianhydrides by either a one-step or a conventional two-step polymerization process.[30] Most of the thermally stable PIs were organosoluble and can be solution cast into tough and flexible films. The **P2** films exhibited two reversible oxidation redox couples and good EC stability with obvious color changes from pale yellowish to green and blue related to their oxidation states.

Afterwards, Liou and Hsiao continuously reported the synthesis of high-performance PIs carrying the TPA or triarylamine derivatives as electroactive functional moieties (Scheme 2). Two series of PIs with piperidine (**P3-a**) and morpholine (**P3-b**) substituents were reported and exhibited lower oxidation potential with enhanced electrochemical stability.[31,32] In addition, bulky *tert*-butyl (**P3-c**) or electron-donating methoxy (**P3-d**) substituents incorporated at the electrochemically active C-3 and C-6 sites of the carbazole unit also could prevent the coupling reactions of carbazoles, resulting in greatly improved redox and EC stability of the obtained PIs.[33]



Scheme 1

Three novel solution-processable PIs **P3e** containing TPA and pendant viologen moieties were prepared from the newly synthesized diamine and three commercially available dianhydrides.[34] The obtained multi-colored EC PI films revealed ambipolar electrochemical behavior with coloration changes from a transmissive neutral state to the cyan/magenta/yellow redox states, implying great potential for application in smart windows and displays.

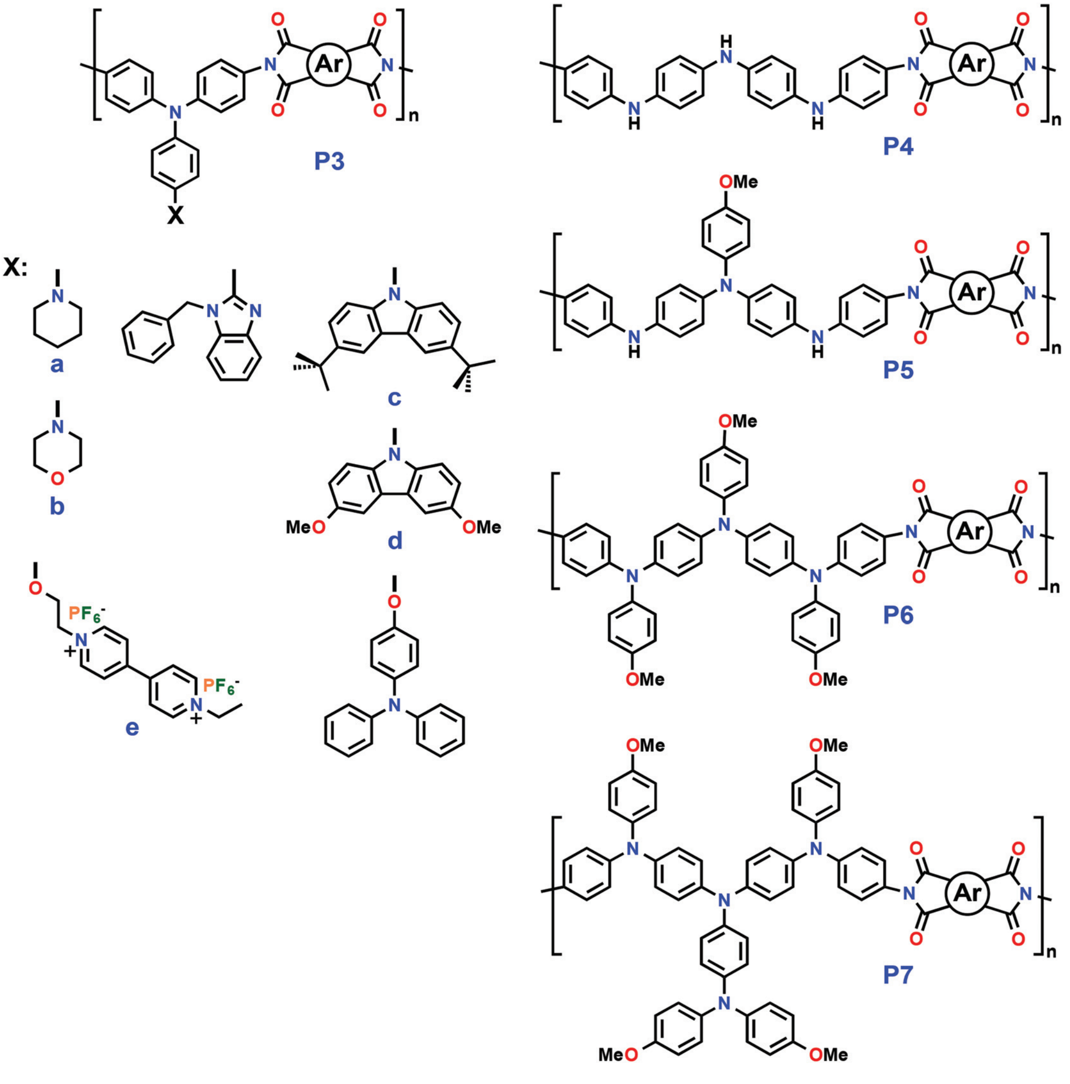
Three series of new ambipolar EC PIs containing aniline derivatives were prepared from the polycondensation of three diamine monomers with different degrees of 4-methoxyphenyl substitution.[35] The series of diphenylamine (DPA)-based PIs, **P4** and **P5**, could not effectively stabilize the cationic radicals of the oxidized form compared to the corresponding TPA-based polymer **P6** due to the lack of the extra phenyl rings for resonance. Furthermore, the lower electrochemical stability of DPA-based PIs **P4** than TPA-based PIs **P6** also could be attributed to the unrecoverable protons at the amino groups in the nonacidic electrolyte solution.

Our group also fabricated flexible and multi-colored EC devices from electroactive aromatic PIs **P7** with a starburst triarylamine unit (Fig. 1).[36,37] The organosoluble PIs **P7** showed useful levels of thermal stability and high glass-transition temperatures. The **P7** films exhibited reversible electrochemical oxidation and electrochromism both in the visible light and near-infrared (NIR) regions with a high contrast ratio, coloration efficiency, low switching time, and outstanding stability for long-term EC operation. These characteristics suggest that the starburst triarylamine-based PIs **P7** have great potential for flexible electronics applications.

3. Triphenylamine-based polyamides

Aromatic polyamides (PAs) are also well known as microelectronic materials due to their outstanding thermal and mechanical resistance. Incorporation of packing-disruptive TPA units into PAs not only could preserve high thermal stability and glass transition temperature, but enhance the solubility and film-forming ability, which is beneficial for the fabrication of large-area optoelectronic devices. PAs **P8** containing TPA groups were first reported in 1990 from 4,4′-diaminoTPA and various dicarboxylic acids by Imai *et al.* *via* the phosphorylation polyamidation (Scheme 3).[38]

To date, Liou, Hsiao,[39–60] and other groups[61–67] have developed various TPA-containing PAs with interesting EC coloring behaviors (Scheme 3). These organosoluble PAs were thermally stable with high glass-transition temperatures. Some of the PA films exhibited good electrochemical reversibility with a high contrast ratio, high coloration efficiency, fast switching properties, and remarkable EC stability.



Scheme 2

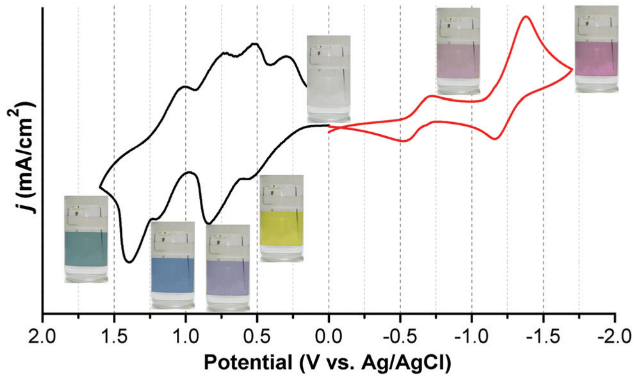
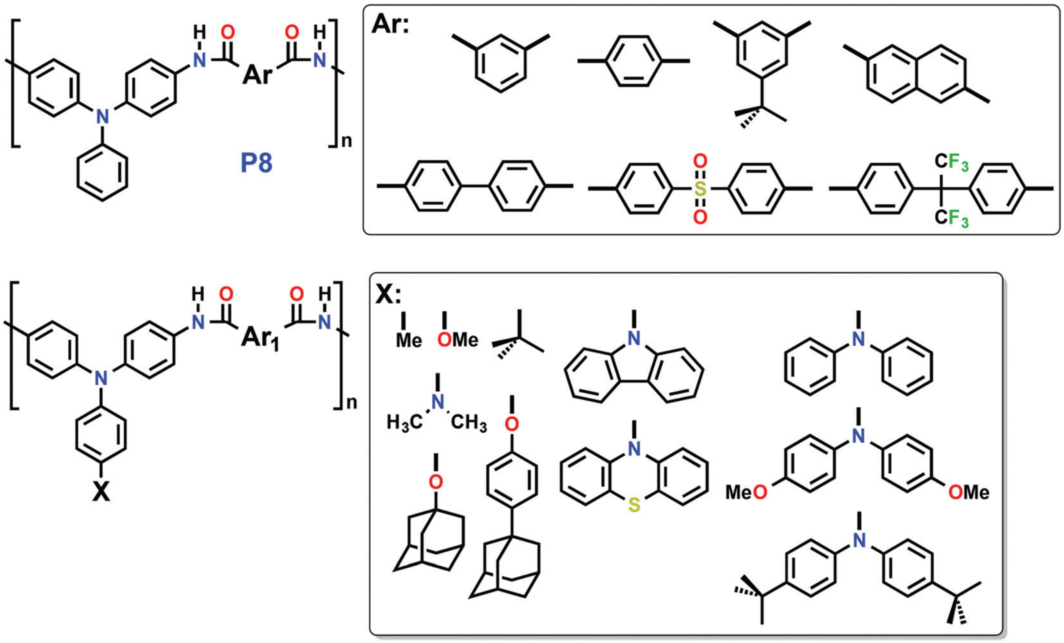


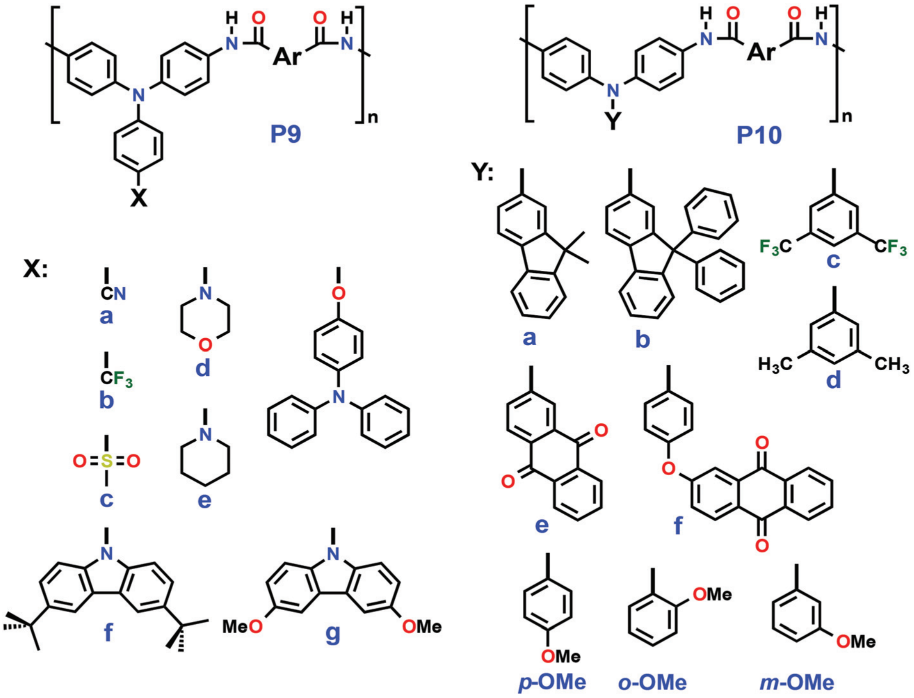
Fig. 1 Cyclic voltammetric diagrams of **P7** and its EC behaviors at various applied potentials. Reproduced from ref. 37 with permission from The Royal Society of Chemistry.

Various electron-donating or electron-withdrawing groups could also be incorporated into TPA-based PAs. The electro-withdrawing group, such as cyano (**P9-a**),[50] trifluoromethyl (**P9-b**),[57] and methylsulfonyl (**P9-c**),[66] substituted TPA-based PAs exhibited higher oxidation potentials while increasing the optical transparency and high contrast ratio in the visible light range. Besides, electron-donating groups, piperidine (**P9-d**)[56] and morpholine (**P9-e**),[55] were also incorporated to reduce the oxidation potential and increase the electrochemical stability of the resulting PAs (Scheme 4).

By incorporating bulky *tert*-butyl (**P9-f**) or electron-donating methoxy (**P9-g**) units into the electrochemically active sites, C-3 and C-6 of the carbazole units, the coupling reactions of carbazoles could be effectively prevented (Fig. 2).[6,53] Thus, the obtained PAs revealed valuable EC characteristics such as enhanced absorption in the NIR region, green/blue EC coloring changes, fast switching behaviors, and high electrochemical/EC reversibility.



Scheme 3



Scheme 4

A series of fluorescent PAs, **P10-a** and **P10-b**, with fluorene-based TPA units in the backbone were prepared and applied as EC and electrofluorescent dual-switching materials.[61,63,65] The obtained polymer films revealed high EC coloration efficiency and exhibited EC stability over continuous 500 cycles. The introduction of an electron-withdrawing $-CF_3$ group increased the oxidation potential of the PAs **P10-c** and decreased the electrochemical and EC stability of the PAs,[57,58,60] while the CH_3TPA-containing PAs **P10-d** exhibited higher redox stability.

Two series of EC TPA-based PAs with anthraquinone (AQ) units (**P10-e**) and additional phenoxy linkage (**P10-f**) were

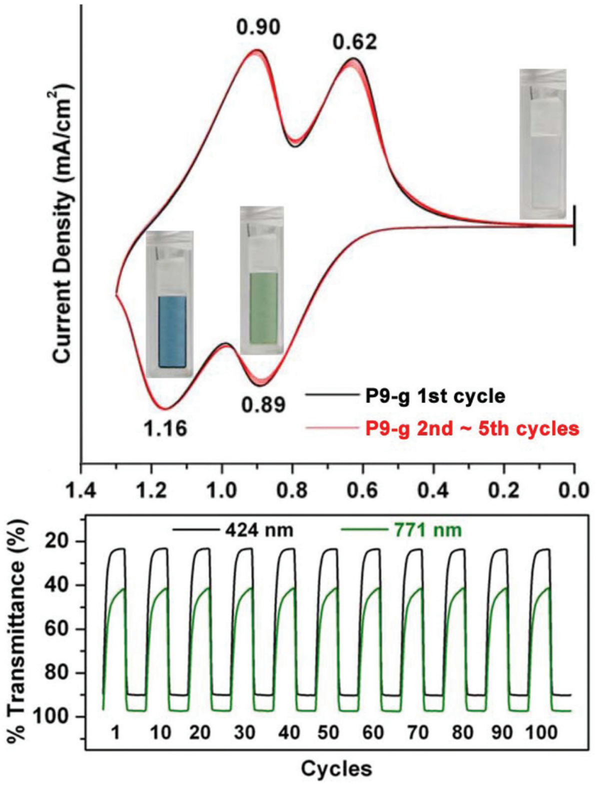


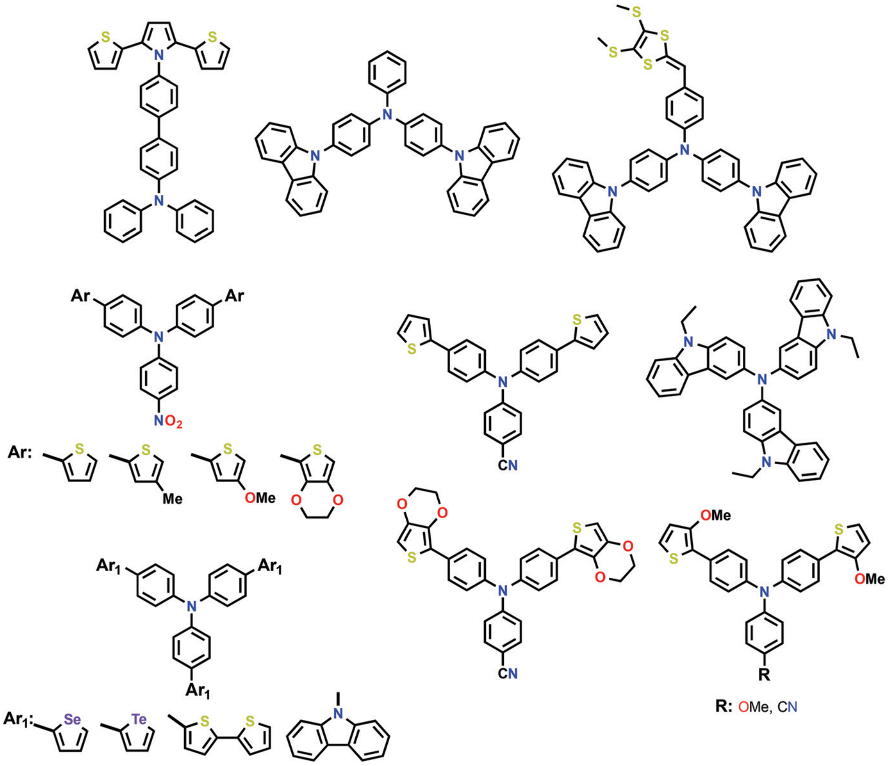
Fig. 2 CV diagrams and potential step absorptometry of the PA **P9-g** film as well as the EC behaviors. Reproduced from ref. 53 with permission of Wiley Interscience.

readily synthesized *via* low-temperature solution polycondensation.[49] In addition to high T_g, thermal stability and good solubility, these PAs revealed valuable ambipolar and reversible redox couples with a high contrast ratio both in the visible range and the NIR region.

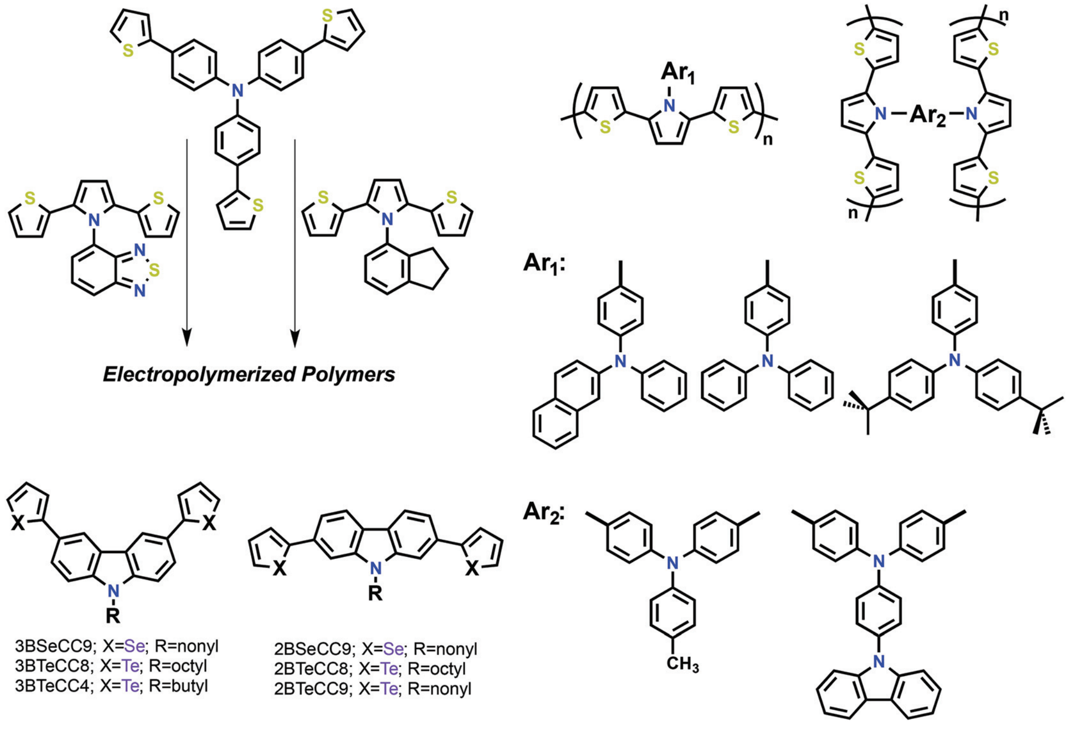
Three TPA-based diamine monomers with methoxy substituents at the *ortho*, *meta*, and *para* positions, respectively, were also synthesized.[62] The energy band gap and oxidation onset potential (E_{onset}) of the corresponding PA films were in the order of **P10-*p*-OMe** < **P10-*o*-OMe** < **P10-*m*-OMe**. In addition, the different EC behaviors of PAs **P10** were also measured and discussed according to the chemical structures of different diamines.

4. Electropolymerized poly(triphenylamine)s

Liou and Hsiao have reported that introducing electron-donating species as protecting groups to triarylamine moieties can efficiently prevent the well-known formation of TPB[68,69] from the unstable cation radical of TPA moieties through tail to tail coupling, while the coupling reaction can be used to design electropolymerizable monomers by attaching two or more unsubstituted TPA or carbazole units into an electron-withdrawing core. In addition, TPA as the core can also be fused with thiophene, ethylenedioxythiophene, dithienylpyrrole, and chalcogenophene (Se, Te) derivatives *via* an electrochemical process (Schemes 5 and 6).[70–79] Carbazole is another type of



Scheme 5



Scheme 6

arylamine with dehydrocyclized diphenylamine at the *ortho* position of the diphenyl group, and the substituent effects of carbazole and its *N*-substituted derivatives were first studied systematically by Ambrose and Nelson in 1968.[80] The electropolymerization of unprotected TPA and *N*-phenylcarbazole compounds *via* the oxidative dimerization reaction has been efficiently employed to provide the unique advantages by combining both one-step facile synthesis and direct fabrication of electroactive polymer films on the electrode surface. Hsiao's group first reported a series of TPA and *N*-phenylcarbazole compounds with amide, imide, and ester units to achieve the EC polymer films *via* this facile electropolymerization (Scheme 7).[52,81–86]

Besides, amide and imide functional groups can also act as linkages between TPA, carbazole and triptycene/AQ groups as precursors of new EC polymers (Scheme 8).[87,88] The electropolymerization approach significantly saves the experimental time and solves the solubility problems that are usually encountered with the conventional methods. Notably, the ambipolar polymers with imide and TPA moieties exhibited interesting multi-color EC behaviors and thus could enlarge the scope for EC applications.

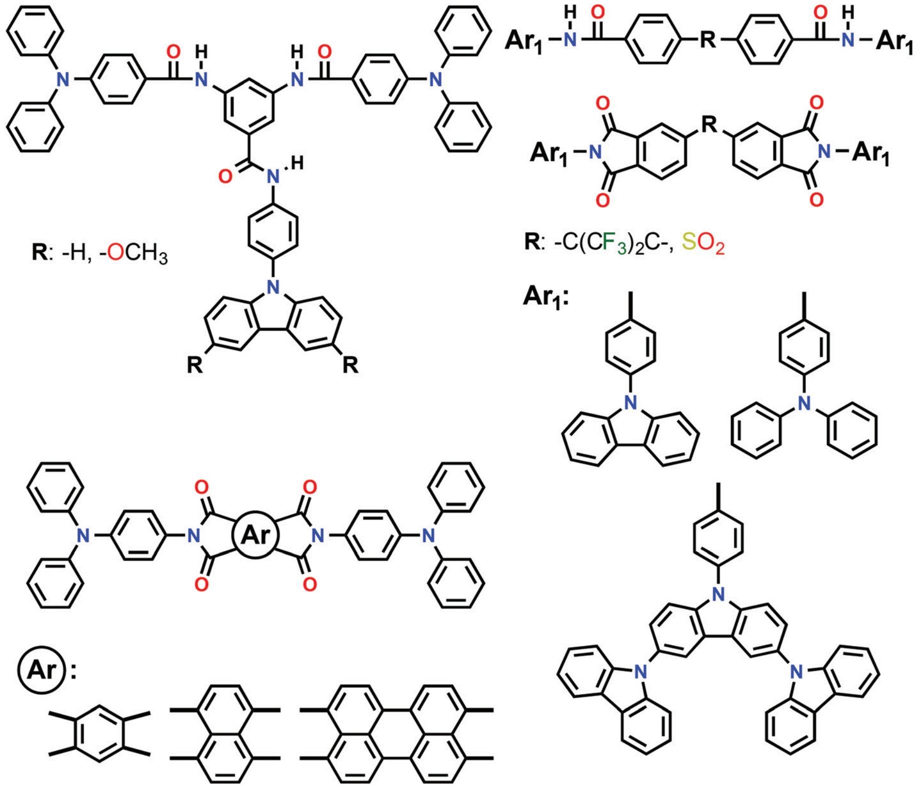
5. Triphenylamine-based conjugate polymers

Four TPA-based conjugate polymers **P11** were synthesized and applied in EC devices (Scheme 9).[89] The obtained conjugated polymers exhibited good thermal stabilities with the color changes from neutral to oxidized form as follows (Fig. 3): orange to dark green for **P11a**; light yellow to reddish brown for **P11b**; light blue to grey for **P11c**; and green to bluish green for **P11d**.

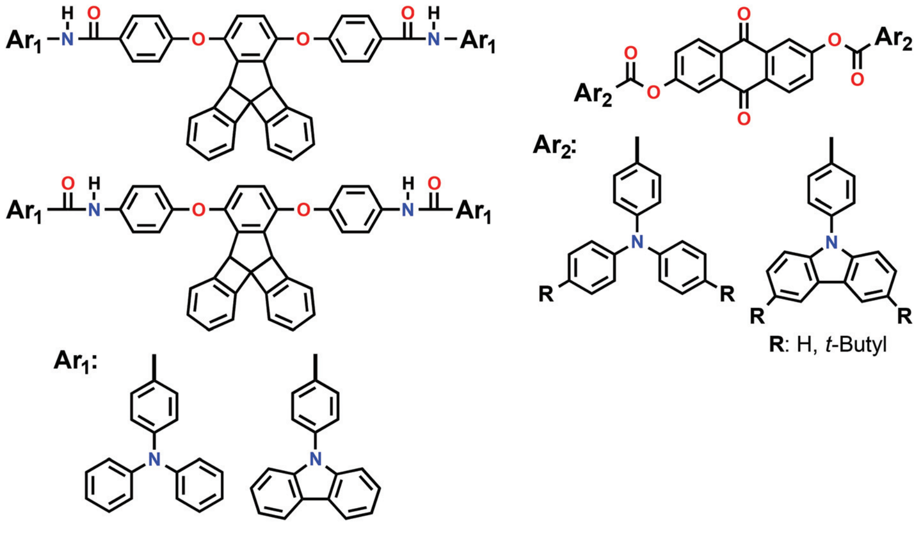
Skene *et al.* prepared **P12** by immobilizing a monomer composed of a TPA-based benzothiadiazole core with two styrene pendant moieties on ITO-coated glass substrates.[90] The immobilized **P12** film was 15% thinner than the corresponding monomer deposited by spray-/spin-coating. The typical absorption of **P12** at 460 nm bleached after oxidization with a broad absorption centered at 880 nm and color changes from yellow to gray, which is similar to its monomer.

Toppare's group synthesized a series of copolymers **P13** and **P14** based on TPA, benzotriazole, and thiophene *via* Stille coupling. The organosoluble polymers with high film-forming quality were used to investigate the effect of the TPA unit and π-bridges on electrochemical/EC properties.[91] The oxidation potentials were significantly affected by the π-bridges and electron density of the polymer backbone.

Xu reported two series of donor–π-bridge–acceptor type conjugated polymers **P15**[92] and **P16**[93] by using Stille coupling polymerization. As shown in Scheme 10, the pendant aldehyde group could be further converted to cyanoacetic acid for obtaining another cyano-pendant polymer. Each of the new polymers is soluble in organic solvents and can be cast onto glass or flexible substrates. The polymers with different electrophilic groups exhibited different EC behaviors, including color changes, driving voltages, and transmittances. With the



Scheme 7

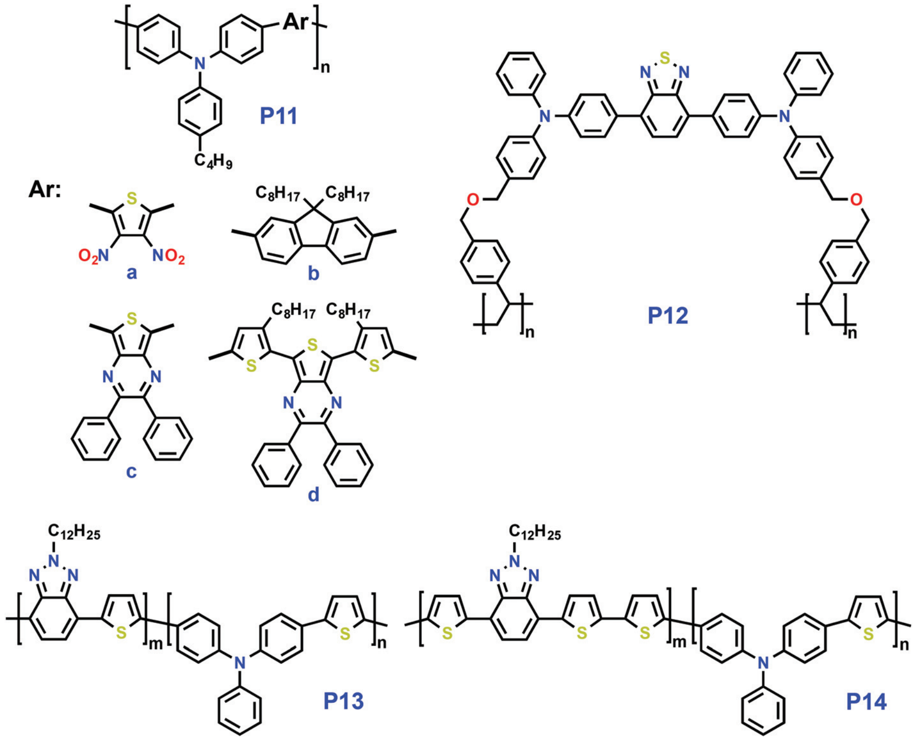


Scheme 8

contribution of counter electrodes, devices derived from polymers with similar color changes could be merged to generate higher optical contrast than their corresponding single polymer film.

A novel conjugated polymer **P17** with bulky hexaphenylbenzene and pyrene fluorescent moieties was successfully prepared by Liaw *et al.*[94] and exhibited noticeable solvatochromic behavior. The anodically EC behavior of **P17** on the ITO-glass or graphene-PET substrates was also well-developed and revealed intense NIR absorption.

The synthesis of conjugated polymer **P18** grafted side chains of oligo-*N*-(2-hydroxyethyl)carbazolyl methacrylate was performed in two steps.[95] A macro-monomer containing dibromo-TPA as an end group was first prepared for atom-



Scheme 9

transfer radical polymerization with *N*-(2-hydroxyethyl)carbazolyl methacrylate, and then further reacted with 9,9-dioctylfluorene-2,7-diboronic acid by the Suzuki polycondensation. Cyclic voltammetry showed that the redox processes were accompanied by the dimerization of carbazole pendant groups thus forming an insoluble crosslinking network. Therefore, this polymer **P18** could be post-modified by electrochemical oxidation and result in EC materials with high solvent resistance.

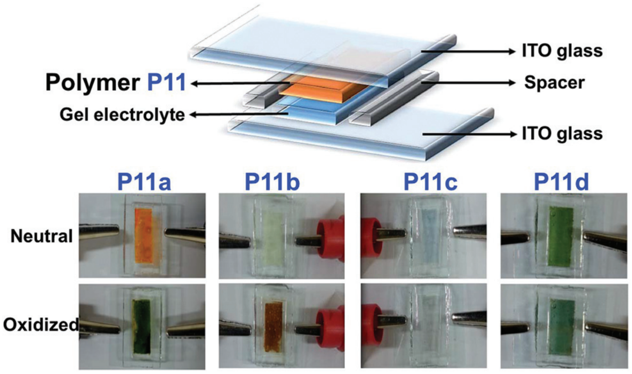


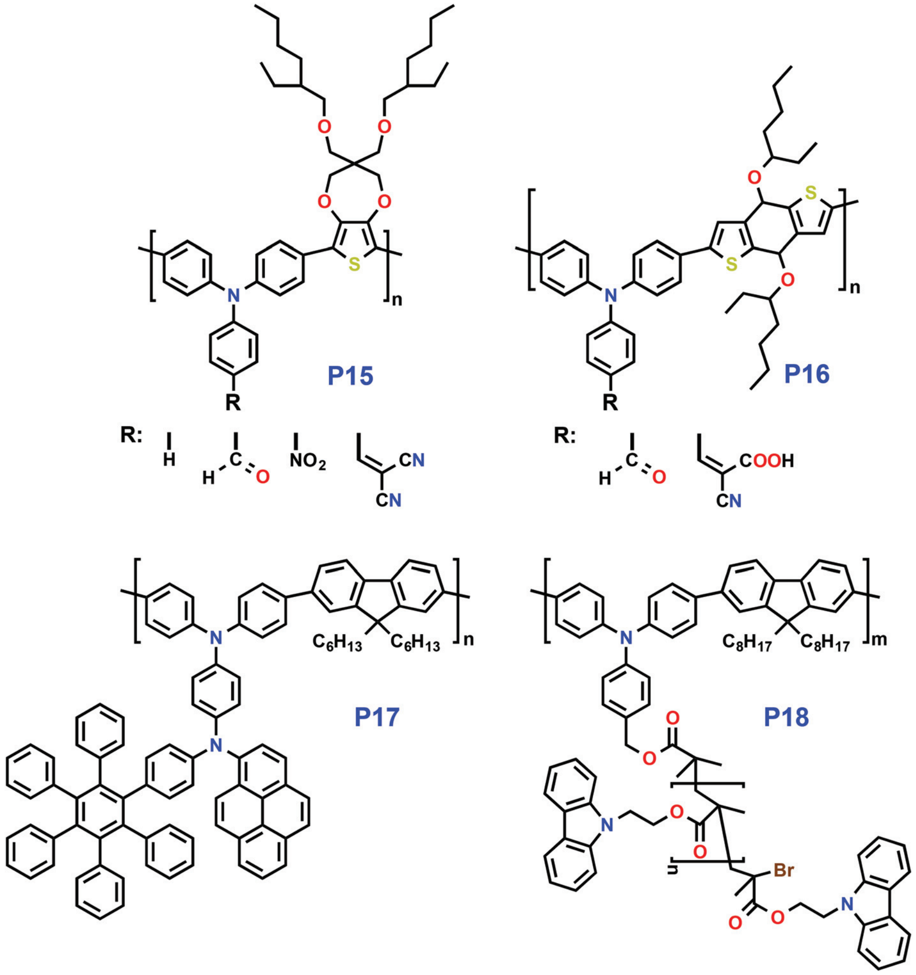
Fig. 3 Schematic configuration of EC cell and EC behaviors of **P11**. Reproduced from ref. 89 with permission from The Royal Society of Chemistry.

6. Other polymers derived from triphenylamine

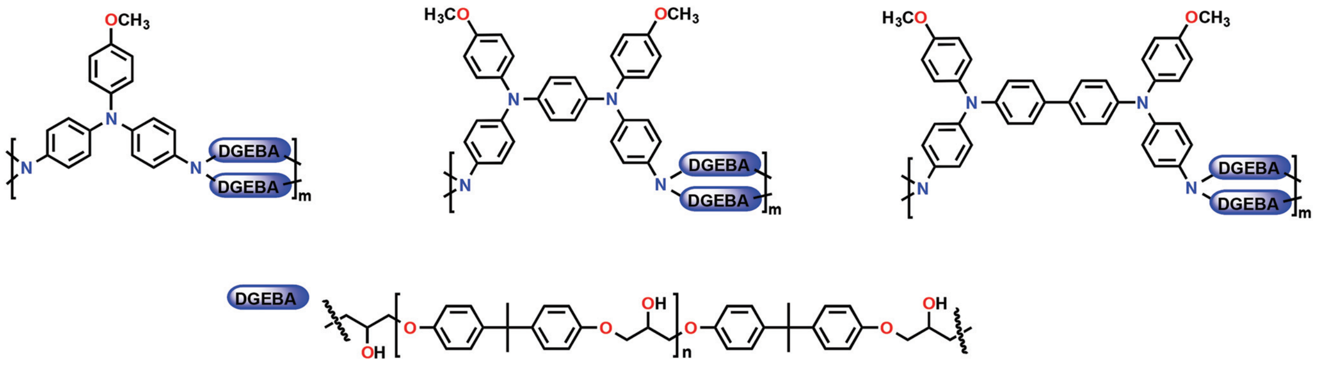
6.1. Epoxy

Epoxy resin is a commercially available material for many industrial applications, such as adhesives, coatings, and composite materials, with valuable properties of excellent adhesion, corrosion resistance, low shrinkage, and toughness.[96] The epoxy groups usually react with amines, isocyanates, mercaptans, phenols, anhydrides, and acids as hardeners to produce thermoset epoxy materials. According to environmental threats, TPA groups have been expected to impart flame retardant behaviors due to their high aromatic content and the resulting systems could be considered as "green" since they are halogen-free and phosphorus-free.

Therefore, our group prepared thermoset epoxy materials with anodically EC characteristics by the thermal curing reaction of the TPA-based diamine monomers with diglycidyl ether of bisphenol A (Scheme 11).[97] These TPA-based EC epoxy materials exhibited good electrochemical stability, multicolored EC, and high optical contrast both in the visible and NIR regions. Furthermore, the absorption in the NIR can also be tuned by adjusting the IV-CT capability of the diamine curing agents. This study successfully opens up the potential optoelectronic application of functional thermoset epoxy materials.



Scheme 10

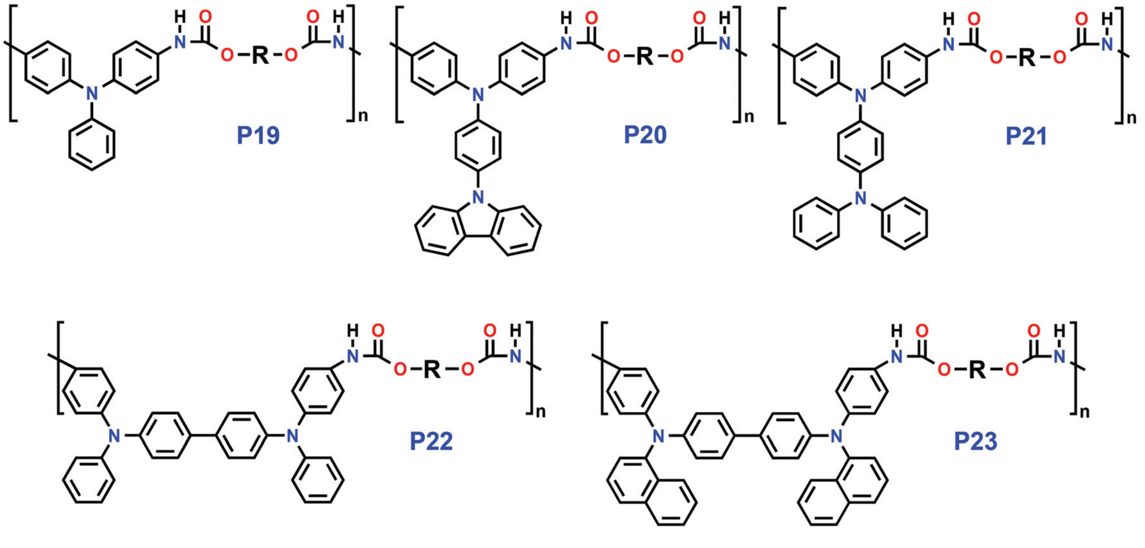


Scheme 11

6.2. Polyurethanes

In the past 30 years, consideration about energy conservation has led high-performance polyurethanes to a worldwide use as thermal insulators, such as flexible substrates, plastic films, textile, coating, and rubber. The broad range of applications was mainly due to their excellent elasticity, abrasion resistance, and extensive substrate suitability.

Recently, several series of TPA-based polyurethanes synthesized by the polycondensation of *N*,*N*-bis(4-isocyanato-



Scheme 12

phenyl)aniline (**P19**), 4,4′-diisocyanato-4″-*N*-carbazolyltriphenylamine (**P20**), *N*,*N*-bis(4-isocyanatophenyl)-*N*′,*N*′-diphenyl-1,4-phenylenediamine (**P21**), *N*′,*N*′-bis(1-naphthyl)-*N*,*N*-bis(4-phenylisocyanate)biphenyl (**P22**) or *N*,*N*′-diphenyl-*N*,*N*′-bis(4-phenylisocyanate)biphenyl (**P23**) with various diphenol monomers were reported by Niu and Wang (Scheme 12).[98–100] The thermally stable polyurethanes exhibited reversible electrochemical behaviors and continuous cycling stability of anodically EC characteristics.

6.3. Polyazomethines

Poly(azomethine)s or poly(Schiff-base)s with a high aromatic content were considered as high performance polymers due to their excellent mechanical strength, high thermal stability, and great potential for optoelectronic applications. Recently, poly(azomethine)s have also been developed for organic electronics, such as light-emitting materials, pH sensors, and metal-collecting materials. Though the insolubility limited their processability and application, our group has successfully incorporated TPA units into poly(azomethine)s **P24** to enhance the solubility and the resultant film-forming ability without sacrificing favorable properties such as high thermal stability or glass transition temperature (Scheme 13).[101]

Skene *et al.* reported that the preparation of polymer **P25** can be directly performed on the working electrode by heating the mixture of monomers.[102] This on-substrate polymerization boosts the advantages of either commercially available or easily synthesized monomers that can be applied for preparing stable electroactive polymers. This method is capable for large-scale fabrication and can also be considered as an environmentally friendly approach because the main by-product is water.

Niu and Bai successfully tuned the band gap of poly(azomethine)s **P26–P29** by copolymerizing the diamines with different dialdehydes.[103–105] The organosoluble poly(azomethine)s showed excellent thermal resistance and reversible EC properties with significant color changes. During electrochemical oxidation or acid doping procedures, the color of poly(azomethine) films can be fine-tuned from initial yellowish to red, violet or blue, suggesting the potential applications of pH sensors, solar cells, and flexible electronic devices.

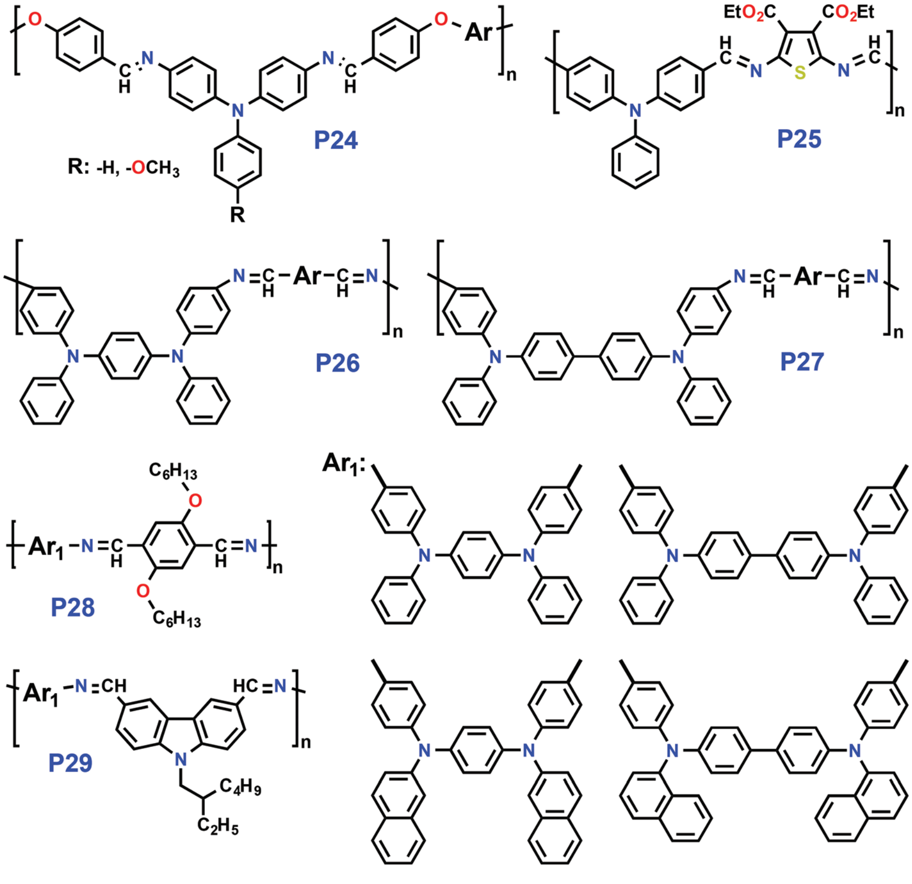
6.4. Polybenzoxazine

Poly(benzoxazine) is a well-developed phenolic material with interesting features to overcome several drawbacks of traditional resole and novolac type phenolic resins, which is widely used in the areas of electrical insulation, electrical encapsulation, and aeronautical and astronautical technologies.

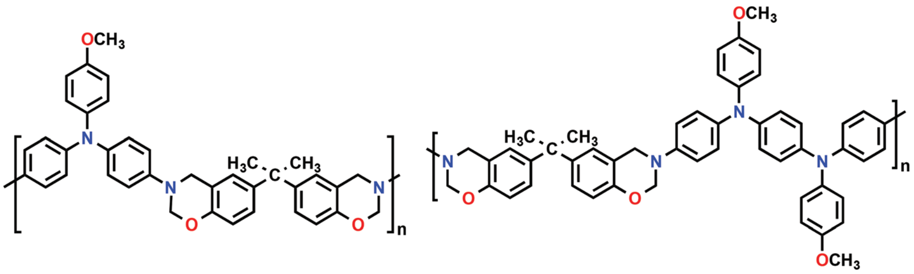
Our group successfully prepared two kinds of TPA-based EC poly(benzoxazine)s by the thermal curing reaction of the corresponding poly(benzoxazine) precursors, which were synthesized by reacting bisphenol A with paraformaldehyde and TPA-based diamines (Scheme 14).[106] These thermally stable TPA-based poly(benzoxazine)s revealed multi-colored EC with high optical contrast in both visible and NIR regions. Compared to the corresponding PAs, these two TPA-based poly(benzoxazine) precursors revealed increased oxidation stages and lower oxidative potentials.

6.5. Polysiloxane

Niu and Wang reported a series of TPA-based polysiloxanes synthesized by a normal hydrosilylation through poly(methylhydrosiloxane) with four TPA-based alkenes (Scheme 15).[107] Grafting TPA onto polysiloxanes was employed as a strategy to ameliorate the thermal stability and EC stability due to the enhanced adhesion between the polymer films and ITO substrate. These polymers can be mixed to generate the other colors based on the color mixing theory. In addition, the electric switching properties of the polymers at 150 °C have been investigated for the first time, indicating high thermal stability



Scheme 13



Scheme 14

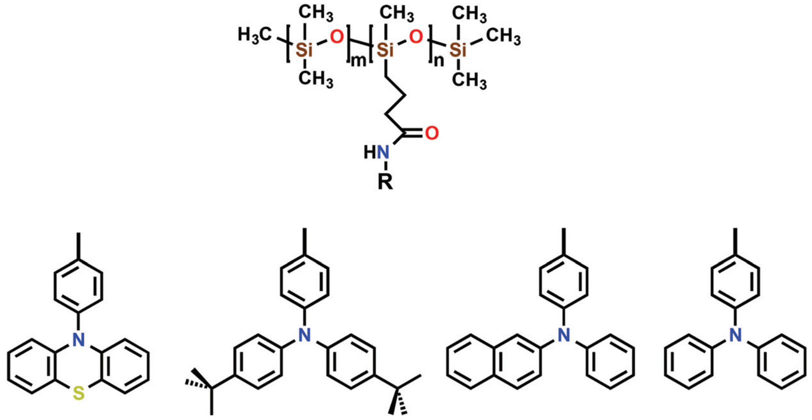
and great potential for relatively high temperature operation and/or long term cycling applications.

6.6. Polymethacrylate

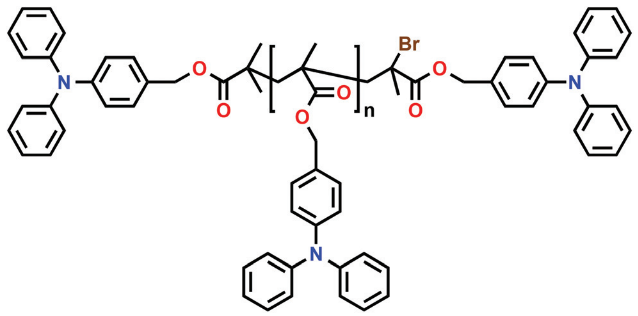
TPA-based polymethacrylate with a well-defined molecular weight and low polydispersity was prepared by atom transfer radical polymerization using 4-(diphenylamino)benzyl-2-bromo-2-methyl-propanoate as an initiator and CuBr/2,2′-bipyridine as a catalytic complex (Scheme 16).[108] The cyclic voltammetric study revealed that the dimerization of TPA pendant groups occurred during redox processes. Consequently, these initial polymers can be post-modified both in solution and bulk states by electrochemical oxidation, leading to a crosslinked and insoluble network with interesting EC behaviors and high coloration efficiency.

6.7. Poly(pyridinium salt)

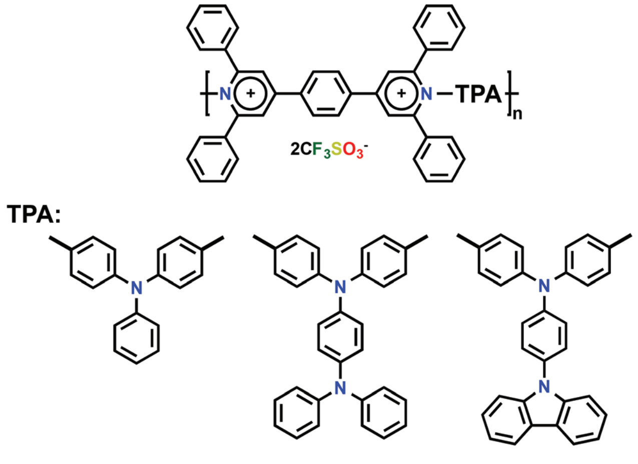
Toppare *et al.* reported a series of new EC conjugated polymeric pyridinium salts containing TPA moieties in the main chain (Scheme 17).[109] The EC properties of the resulting polymer films were investigated by using electrochemical and spectroelectrochemical measurements. The color changes were also studied by colorimetric analyses. The polymer films were highly transmissive at the neutral state and exhibited reversible redox cycles with multi-EC characteristics in the applied potential range of 0–1.2 V.



Scheme 15



Scheme 16



Scheme 17

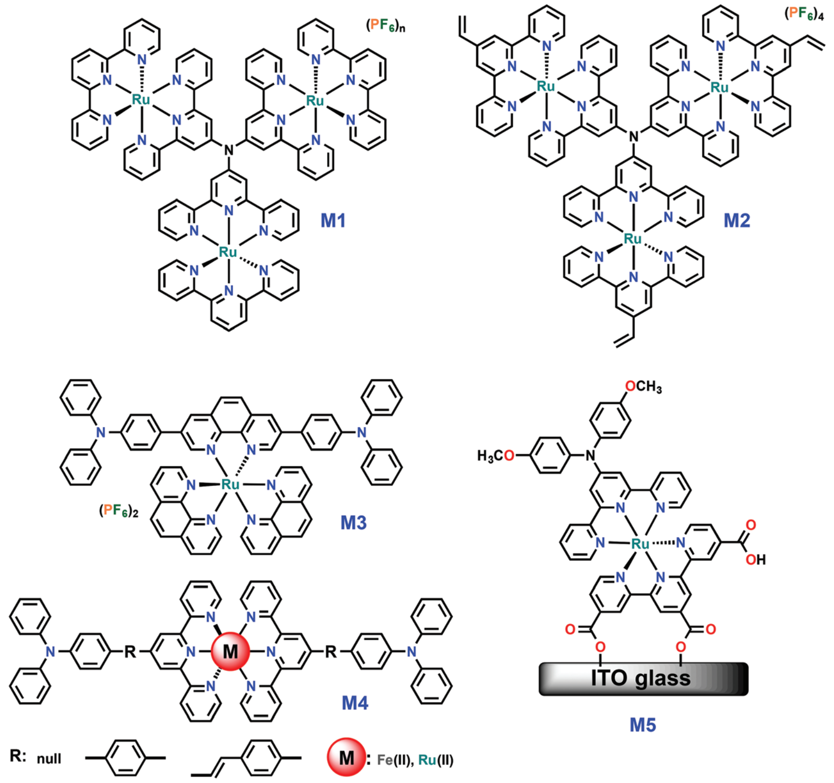
7. Triphenylamine-based metal complexes

Smart switching molecules that exhibit multiple redox processes at low driving voltages with distinguishable redox states have received great attention recently.[110–112] It is also important that the significantly increased information density in the form of multistate memory is promising for information storage applications.[113,114] Until now, the finding and understanding of four or more redox states have been challenging. To obtain multistate redox switches, molecules have to display multiple redox processes at relatively low potentials. More importantly, these solution-based measurements should be converted to surface-confined technologies for practical applications.[115–118]

Polypyridyl ruthenium complexes with a Ru–C bond, denoted as cyclometalated ruthenium complexes, are particularly capable of achieving multistate redox processes in molecular switches.[119,120] The presence of the Ru–C bond in cyclometalated ruthenium complexes could greatly lower the Ru(III/II) potential and give rise to diruthenium[121] or ruthenium-amine[122–124] complexes with three redox states. These complexes with strong absorptions in the visible and NIR regions are promising as EC materials for fiber-optic communications.[125–130]

Recently, Zhong *et al.* have successfully prepared a star-shaped tris-cyclometalated ruthenium complex **M1** with a redox-active triarylamine core, which showed four redox states in a low potential region (Scheme 18).[131] The complex **M1** and the electropolymerized films of the vinyl-functionalized complex **M2** both displayed four consecutive one-electron anodic redox couples at low potentials, functioning as a molecular redox switch with up to five well-separated states. In addition, a high contrast ratio of 63% was achieved at the optic telecommunication wavelength (1550 nm) (Fig. 4). This is one of the highest contrast ratios ever achieved at this wavelength on the basis of molecular EC materials, and it is potentially useful as active materials for variable optical attenuators in optic telecommunication.

Leung and Su reported a convenient and effective method to access conjugated polymers containing electron donating-accepting pairs from a TPA-based ruthenium complex **M3**.[11] The diphenylamino group in **M3** is beneficial for electropolymerization to give donor–acceptor polymers, and the resulting polymerized-**M3** also demonstrated interesting EC and photoresponsive behavior.



Scheme 18

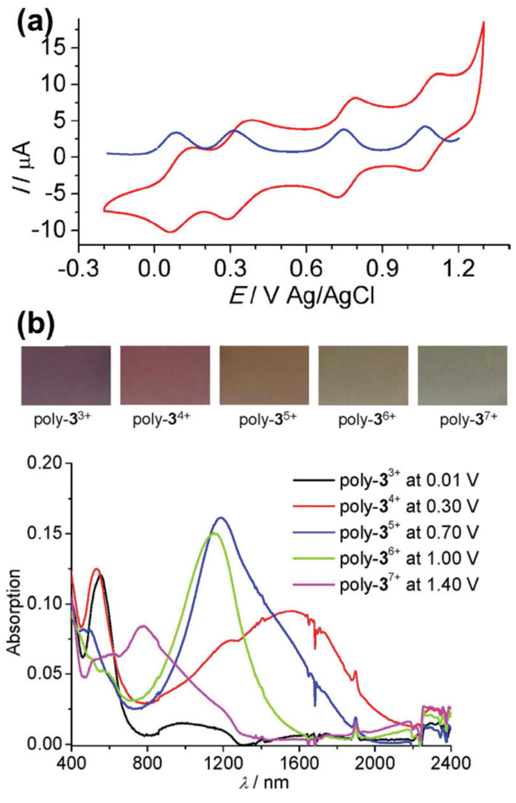


Fig. 4 (a) CV (red curve) and DPV (blue curve) of **M1**. (b) Absorption spectra and photos of the poly-**M2**$^{n+}$/ITO film at different redox states. Reproduced from ref. 133 with permission of Springer Nature.

Zhong also designed and synthesized six metallic terpyridine-based complexes **M4** with two TPA end groups that could produce four terminal active sites for the purpose of following electrochemical polymerization.[132] Interestingly, the EC memory ability was found depending on both the rigidity and length of these TPA-based moieties. Meanwhile, the TPA-based moieties with more rigid and conjugated linkages could effectively increase intramolecular CT from the TPA group (D) to the metallic terpyridine (A) that is beneficial for stabilizing the oxidized states (*i.e.*, Ru^{3+}, Fe^{3+}) of metallic terpyridine and thus enhance the memory ability of the EC films. In addition, cyclometalated ruthenium complex **M5** with a redox-active arylamine substituent and three carboxylic acid groups also demonstrated feasibility as a self-assembling monolayer on ITO electrode surfaces for fabricating NIR EC three state switching.[130] The obtained monolayer film exhibited intense NIR absorption with long optical retention time at each oxidation state. Thus, this approach can provide an excellent molecular platform for the construction of a surface-confined flip-flop system with high ON/OFF ratios, which is attractive for the preparation of NIR EC and memory devices at the molecular scale.

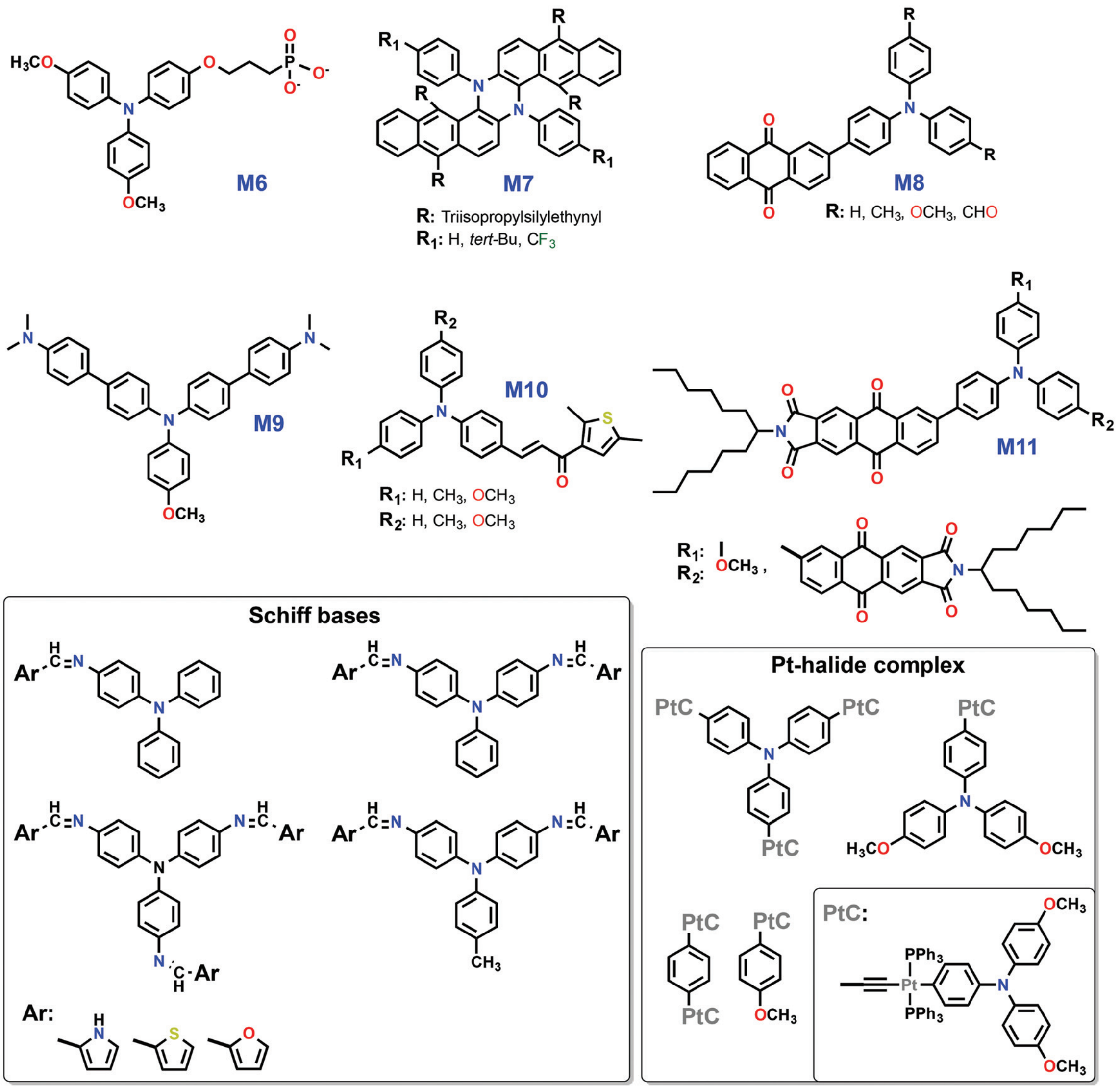
8. Triphenylamine-based molecules

Molecules revealing physical responses under stimuli have been widely investigated as promising functional switching and memory devices.[133,134] Among them, redox-active materials have received great attention due to the prospects as nano-sized electronic devices.[135–141]

The prototype redox-flow EC window employs a TPA derivative **M6** anchored to a mesoporous TiO_2 scaffold as an EC component (Scheme 19).[142] **M6** can be rapidly oxidized in aqueous I_3^- solution to generate the colored form, **M6**$^{\bullet+}$ radical cation, and then reduced back to the original colorless **M6** by aqueous I^- solution. Aqueous I_3^- or I^- electrochemically generated in an external two-compartment cell could be pumped through the window cavity to form the redox-flow EC window between colored and colorless states (Fig. 5).

Hiroto and Shinokubo reported the synthesis of π-extended *N*,*N*′-diaryldihydrophenazines **M7**, which exhibited dramatic conformational and three-state NIR absorption changes by both chemical and electrochemical stimuli.[143] Upon chemical oxidation, the change of optical absorption was confirmed in a two-step procedure, and the NMR analysis demonstrated a conformational change upon oxidation, which was also supported by theoretical calculations. Such molecules with interesting NIR EC behavior and dramatic conformational changes caused by an electrochemical stimulus are promising for applying in low-energy molecular memory and molecular actuator devices.

A series of dyes **M8** with intramolecular CT between AQ and TPA units have been synthesized by the Suzuki reaction, which are ideal candidates as probes for the detection of less polar solvents.[144] The cyclic voltammetry and DFT calculations imply that these dyes could be potentially applied in the wide field of optoelectronics. In addition, the dyes without substituents would be potentially a host for complexation due to the formation of cavity structures in crystals.



Scheme 19

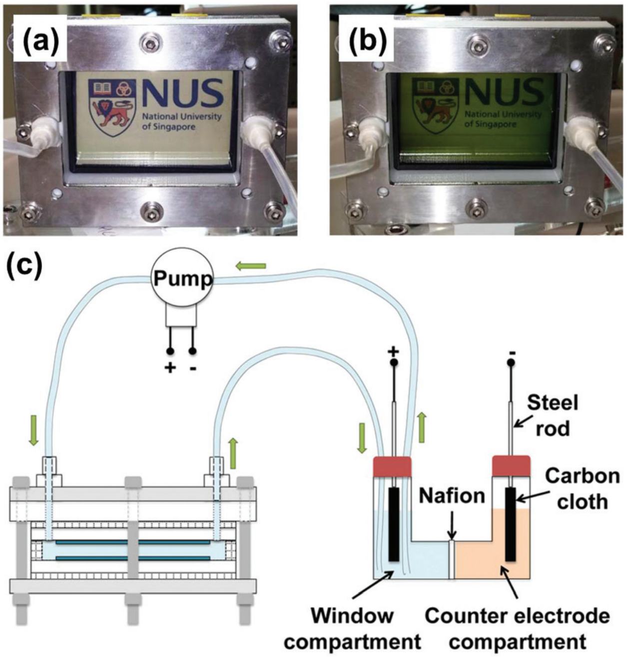


Fig. 5 Photographs of the redox-flow **M6**-based EC window. (a) Decolored state and (b) colored state. (c) Schematic diagram of the redox-flow EC window. Reproduced from ref. 144 with permission of American Chemical Society.

Another TPA derivative **M9** was synthesized by the cross-coupling reaction and its photophysical and electrochemical properties were studied.[145] In order to obtain several redox and protonation states, three amino groups were incorporated into **M9** as well as two biphenyl linkages, which allow an extended electron delocalization and a better stabilization of its redox states. **M9** was found to exhibit three redox states (with EC of colorless, yellow, green, and blue), and three protonated states. In addition, the fluorescence switches at different oxidation and protonation states were also investigated.

A series of TPA-based chalcones **M10** were synthesized by the Aldol reaction and their photophysical, electrochemical, and EC properties were studied.[146] The molecular orbital energy levels and excitation energies were calculated and we found that the fluorescence intensity decreases with the formation of the CT state. The spectroelectrochemical results indicated that **M10** revealed good EC stability with color changes from yellow to blue. By this token, chalcone-containing TPA moiety is another new approach for tuning EC behaviors.

Wan *et al.* reported three D–A molecules **M11** with different AQ imide arms connected to the TPA core.[147] These compounds showed high solubility in common organic solvents due to the propeller-like structures. CV results revealed that all these compounds exhibit three redox peaks, two in the cathodic regime owing to the formation of AQ imide radical anions and dianions, respectively, and one in the positive regime corresponding to the TPA radical cations. Spectroelectrochemical measurements demonstrated that the intramolecular CT absorption could be tuned electrochemically. In addition, the multiple EC color and intensive NIR absorptions can be achieved in one single ambipolar molecule due to the formation of radical cations and radical anions in the oxidation and reduction process, respectively.

TPA-based Schiff bases containing pyrrole, thiophene, or furan moieties were also synthesized and revealed interesting EC behaviors with an obvious color change from pale yellow at neutral form to red at oxidative form. In addition, all the obtained compounds displayed multiple color changes at different pH values and the results showed a perfect linear relationship between the absorption and proton concentration. Thus, these new Schiff bases can be used as proton detection and EC materials due to their sensitive acidochromic properties.[148–150]

In addition, the Pt-ethynyl complexes containing up to four redox-active TPA cores were prepared by oxidative addition followed by the CuI-catalyzed dehydrohalogenation reaction. The complexes undergo a single electrochemical process for each chemically distinct type of TPA in the molecular backbone. The perfect reversibility of the larger systems indicates that they can be used as charge storage materials and are capable of releasing up to four electrons. The combination of electrochemical, spectroelectrochemical, and quantum chemical analyses demonstrated that only a weakly electronic coupling between the amine moieties at the redox states generated from one-electron oxidation.[151]

9. Conclusions

In this review, we mainly summarized the recent development of TPA-based EC materials with emphasis on the synthetic approaches and the resultant EC behaviors. TPA-based EC materials with promising optical and electrical properties are of great potential for practical applications. Based on the excellent and interesting results of these EC materials, we believe that the optimization of their devices could further improve the performance and fully explore the potential of these multicolored EC devices as shutters of transparent displays, smart windows for building construction and aircraft, wearable applications, and electronic tag.

Conflicts of interest

There are no conflicts to declare.

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References

1 C. Lambert and G. Nöll, *Synth. Met.*, 2003, **139**, 57–62.

2 Z. Fang, V. Chellappan, R. D. Webster, L. Ke, T. Zhang, B. Liu and Y.-H. Lai, *J. Mater. Chem.*, 2012, **22**, 15397–15404.

3 M.-Y. Chou, M.-K. Leung, Y. O. Su, C. L. Chiang, C.-C. Lin, J.-H. Liu, C.-K. Kuo and C.-Y. Mou, *Chem. Mater.*, 2004, **16**, 654–661.

4 K.-Y. Chiu, T.-X. Su, J.-H. Li, T.-H. Lin, G.-S. Liou and S.-H. Cheng, *J. Electroanal. Chem.*, 2005, **575**, 95–101.

5 J. Natera, L. Otero, L. Sereno, F. Fungo, N.-S. Wang, Y.-M. Tsai, T.-Y. Hwu and K.-T. Wong, *Macromolecules*, 2007, **40**, 4456–4463.

6 S.-H. Hsiao, H.-M. Wang and S.-H. Liao, *Polym. Chem.*, 2014, **5**, 2473.

7 C. Quinton, V. Alain-Rizzo, C. Dumas-Verdes, F. Miomandre, G. Clavier and P. Audebert, *RSC Adv.*, 2014, **4**, 34332–34342.

8 D. Sek, B. Jarzabek, E. Grabiec, B. Kaczmarczyk, H. Janeczek, A. Sikora, A. Hreniak, M. Palewicz, M. Lapkowski, K. Karon and A. Iwan, *Synth. Met.*, 2010, **160**, 2065–2076.

9 Y. Oishi, H. Takado, M. Yoneyama, M.-A. Kakimoto and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.*, 1990, **28**, 1763–1769.

10 G.-S. Liou, S.-H. Hsiao, M. Ishida, M. Kakimoto and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 3815–3822.

11 M.-K. Leung, M.-Y. Chou, Y. O. Su, C. L. Chiang, H.-L. Chen, C. F. Yang, C.-C. Yang, C.-C. Lin and H.-T. Chen, *Org. Lett.*, 2003, **5**, 839–842.

12 P. Monk, R. Mortimer and D. Rosseinsky, in *Electrochromism and Electrochromic Devices*, ed. D. Rosseinsky, P. Monk and R. Mortimer, Cambridge University Press, Cambridge, 2007, pp. 1–24.

13 H.-J. Yen and G.-S. Liou, *Polym. Chem.*, 2012, **3**, 255–264.

14 V. L. Bell, B. L. Stump and H. Gager, *J. Polym. Sci., Polym. Chem. Ed.*, 1976, **14**, 2275–2291.

15 P. E. Cassidy, *Thermally Stable Polymers: Synthesis and Properties*, Marcel Dekker, New York, 1980.

16 T. L. S. Clair and D. A. Yamaki, *U. S. Pat.*, 4398021, 1983.

17 T. L. S. Clair and D. A. Yamaki, *U. S. Pat.*, 4489027, 1984.

18 P. M. Hergenrother, *Angew. Makromol. Chem.*, 1986, **145**, 323–341.

19 D. Wilson, H. D. Stenzenberger and P. M. Hergenrother, *Polyimides*, Springer Netherlands, New York, 1990.

20 H. Yang, *Kevlar aramid fiber*, John Wiley & Sons, New York, 1993.

21 M. K. Ghosh and K. L. Mittal, *Polyimides: Fundamentals and Applications*, Marcel Dekker, New York, 1996.

22 J. de Abajo and J. G. de la Campa, in *Progress in Polyimide Chemistry I*, ed. H. R. Kricheldorf, Springer Berlin Heidelberg, 1999, vol. 140, ch. 2, pp. 23–59.

23 K. L. Mittal, *Polyimides: Synthesis, Characterization, and Applications*, Plenum, New York, 1984.

24 H. H. Yang, *Aromatic High-Strength Fibers*, John Wiley & Sons, Inc., New York, 1989.

25 M. J. M. Abadie and B. Mittal, *Polyimides and Other High Temperature Polymers*, Elsevier, Amsterdam, 1991.

26 P. E. Cassidy, *Thermally Stable Polymers*, Marcel Dekker, New York, 1980.

27 Y. Oishi, M. Ishida, M.-A. Kakimoto, Y. Imai and T. Kurosaki, *J. Polym. Sci., Part A: Polym. Chem.*, 1992, **30**, 1027–1035.

28 K.-I. Okamoto, K. Tanaka, H. Kita, M. Ishida, M. Kakimoto and Y. Imai, *Polym. J.*, 1992, **24**, 451–457.

29 N. A. Vasilenko, Y. I. Akhmet'eva, Y. B. Sviridov, V. I. Berendyayev, Y. D. Rogozhkina, O. F. Alkayeva, K. K. Koshelev, A. L. Izyumnikov and B. V. Kotov, *Polym. Sci. USSR*, 1991, **33**, 1439–1450.

30 S.-H. Cheng, S.-H. Hsiao, T.-H. Su and G.-S. Liou, *Macromolecules*, 2005, **38**, 307–316.

31 S.-H. Hsiao and Y.-H. Hsiao, *High Perform. Polym.*, 2017, **29**, 431–440.

32 S.-H. Hsiao, Y.-H. Hsiao and Y.-R. Kung, *J. Electroanal. Chem.*, 2016, **764**, 31–37.

33 H.-M. Wang and S.-H. Hsiao, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, **52**, 1172–1184.

34 H. J. Yen, C. L. Tsai, S. H. Chen and G. S. Liou, *Macromol. Rapid Commun.*, 2017, **38**, 1600715.

35 L.-T. Huang, H.-J. Yen and G.-S. Liou, *Macromolecules*, 2011, **44**, 9595–9610.

36 H. J. Yen, C. J. Chen and G. S. Liou, *Adv. Funct. Mater.*, 2013, **23**, 5307–5316.

37 C.-J. Chen, H.-J. Yen, Y.-C. Hu and G.-S. Liou, *J. Mater. Chem. C*, 2013, **1**, 7623.

38 Y. Oishi, H. Takado, M. Yoneyama, M.-A. Kakimoto and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.*, 1990, **28**, 1763–1769.

39 S.-H. Hsiao, Y.-M. Chang, H.-W. Chen and G.-S. Liou, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 4579–4592.

40 G.-S. Liou, H.-W. Chen and H.-J. Yen, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 4108–4121.

41 C.-W. Chang, G.-S. Liou and S.-H. Hsiao, *J. Mater. Chem.*, 2007, **17**, 1007–1015.

42 S.-H. Hsiao, G.-S. Liou, Y.-C. Kung and H.-J. Yen, *Macromolecules*, 2008, **41**, 2800–2808.

43 S.-H. Hsiao, G.-S. Liou, Y.-C. Kung, H.-Y. Pan and C.-H. Kuo, *Eur. Polym. J.*, 2009, **45**, 2234–2248.

44 Y.-C. Kung, G.-S. Liou and S.-H. Hsiao, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 1740–1755.

45 S.-H. Hsiao, G.-S. Liou, Y.-C. Kung and T.-J. Hsiung, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 3392–3401.

46 H.-J. Yen, S.-M. Guo and G.-S. Liou, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 5271–5281.

47 H.-J. Yen and G.-S. Liou, *J. Mater. Chem.*, 2010, **20**, 9886.

48 L.-T. Huang, H.-J. Yen, J.-H. Wu and G.-S. Liou, *Org. Electron.*, 2012, **13**, 840–849.

49 H.-J. Yen, K.-Y. Lin and G.-S. Liou, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 61–69.

50 H. J. Yen and G. S. Liou, *Chem. Commun.*, 2013, **49**, 9797–9799.

51 S.-H. Hsiao and Y.-T. Chou, *Macromol. Chem. Phys.*, 2014, **215**, 958–970.

52 S.-H. Hsiao and J.-W. Lin, *Polym. Chem.*, 2014, **5**, 6770–6778.

53 H.-M. Wang and S.-H. Hsiao, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, **52**, 272–286.

54 S.-H. Hsiao and S.-L. Cheng, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**, 496–510.

55 S.-H. Hsiao, Y.-H. Hsiao and Y.-R. Kung, *J. Polym. Sci., Part A: Polym. Chem.*, 2016, **54**, 1289–1298.

56 S.-H. Hsiao, Y.-H. Hsiao, Y.-R. Kung, C.-M. Leu and T.-M. Lee, *React. Funct. Polym.*, 2016, **108**, 54–62.

57 S.-H. Hsiao and K.-H. Lin, *J. Fluorine Chem.*, 2016, **188**, 33–42.

58 S.-H. Hsiao and C.-N. Wu, *J. Electroanal. Chem.*, 2016, **776**, 139–147.

59 S.-H. Hsiao and J.-S. Han, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 1409–1421.

60 S.-H. Hsiao and C.-N. Wu, *Polym. Int.*, 2017, **66**, 916–924.

61 N. Sun, F. Feng, D. Wang, Z. Zhou, Y. Guan, G. Dang, H. Zhou, C. Chen and X. Zhao, *RSC Adv.*, 2015, **5**, 88181–88190.

62 M. J. Lee, Y. J. Kwak, W. C. Seok and S. W. Lee, *Polym. Bull.*, 2016, **73**, 2427–2438.

63 N. Sun, S. Meng, D. Chao, Z. Zhou, Y. Du, D. Wang, X. Zhao, H. Zhou and C. Chen, *Polym. Chem.*, 2016, **7**, 6055–6063.

64 N. Sun, S. Meng, Z. Zhou, J. Yao, Y. Du, D. Wang, X. Zhao, H. Zhou and C. Chen, *RSC Adv.*, 2016, **6**, 66288–66296.

65 N. Sun, Z. Zhou, D. Chao, X. Chu, Y. Du, X. Zhao, D. Wang and C. Chen, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 213–222.

66 N. Sun, Z. Zhou, S. Meng, D. Chao, X. Chu, X. Zhao, D. Wang, H. Zhou and C. Chen, *Dyes Pigm.*, 2017, **141**, 356–362.

67 S. Wang, X. Wu, X. Zhang, H. Niu, C. Wang, Y. Zhang, X. Bai, W. Wang and Y. Hou, *Eur. Polym. J.*, 2017, **93**, 368–381.

68 R. R. Nelson and R. N. Adams, *J. Am. Chem. Soc.*, 1968, **90**, 3925–3930.

69 E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy and R. N. Adams, *J. Am. Chem. Soc.*, 1966, **88**, 3498–3503.

70 S. Cai, H. Wen, S. Wang, H. Niu, C. Wang, X. Jiang, X. Bai and W. Wang, *Electrochim. Acta*, 2017, **228**, 332–342.

71 K. Karon, M. Lapkowski, A. Dabuliene, A. Tomkeviciene, N. Kostiv and J. V. Grazulevicius, *Electrochim. Acta*, 2015, **154**, 119–127.

72 X. Lv, S. Yan, Y. Dai, M. Ouyang, Y. Yang, P. Yu and C. Zhang, *Electrochim. Acta*, 2015, **186**, 85–94.

73 P. Zhou, Z. Wan, Y. Liu, C. Jia, X. Weng, J. Xie and L. Deng, *Electrochim. Acta*, 2016, **190**, 1015–1024.

74 Y. Hou, L. Kong, X. Ju, X. Liu, J. Zhao and Q. Niu, *Materials*, 2016, **9**, 779.

75 J.-C. Lai, X.-R. Lu, B.-T. Qu, F. Liu, C.-H. Li and X.-Z. You, *Org. Electron.*, 2014, **15**, 3735–3745.

76 S. Li, G. Liu, X. Ju, Y. Zhang and J. Zhao, *Polymer*, 2017, **9**, 173.

77 T.-Y. Wu and H.-H. Chung, *Polymer*, 2016, **8**, 206.

78 X. Yang, M. Wang, J. Zhao, C. Cui, S. Wang and J. Liu, *J. Electroanal. Chem.*, 2014, **714–715**, 1–10.

79 P. Pander, R. Motyka, P. Zassowski, M. Lapkowski, A. Swist and P. Data, *J. Phys. Chem. C*, 2017, **121**, 11027–11036.

80 J. F. Ambrose and R. F. Nelson, *J. Electrochem. Soc.*, 1968, **115**, 1159–1164.

81 S.-H. Hsiao and Y.-Z. Chen, *Dyes Pigm.*, 2017, **144**, 173–183.

82 S.-H. Hsiao and Y.-Z. Chen, *J. Electroanal. Chem.*, 2017, **799**, 417–423.

83 S.-H. Hsiao and S.-W. Lin, *J. Mater. Chem. C*, 2016, **4**, 1271–1280.

84 S.-H. Hsiao and H.-M. Wang, *J. Polym. Sci., Part A: Polym. Chem.*, 2016, **54**, 2476–2485.

85 S.-H. Hsiao and J.-W. Lin, *Macromol. Chem. Phys.*, 2014, **215**, 1525–1532.

86 S.-H. Hsiao and H.-M. Wang, *RSC Adv.*, 2016, **6**, 43470–43479.

87 S.-H. Hsiao and J.-Y. Lin, *J. Polym. Sci., Part A: Polym. Chem.*, 2016, **54**, 644–655.

88 S.-H. Hsiao and Y.-T. Chiu, *RSC Adv.*, 2015, **5**, 90941–90951.

89 J. Jeong, R. S. Kumar, M. Naveen and Y. A. Son, *RSC Adv.*, 2016, **6**, 78984–78993.

90 M. Wałęsa-Chorab and W. G. Skene, *ACS Appl. Mater. Interfaces*, 2017, **9**, 21524–21531.

91 S. O. Hacioglu, S. Toksabay, M. Sendur and L. Toppare, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, **52**, 537–544.

92 S. Mi, J. C. Wu, J. Liu, J. M. Zheng and C. Y. Xu, *Org. Electron.*, 2015, **23**, 116–123.

93 Q. Du, Y. X. Wei, J. M. Zheng and C. Y. Xu, *Electrochim. Acta*, 2014, **132**, 258–264.

94 P. I. Wang, W. R. Shie, J. C. Jiang, L. J. Li and D. J. Liaw, *Polym. Chem.*, 2016, **7**, 1505–1516.

95 O. I. Negru and M. Grigoras, *J. Polym. Res.*, 2014, **22**, 637.

96 H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967.

97 Y.-W. Chuang, H.-J. Yen, J.-H. Wu and G.-S. Liou, *ACS Appl. Mater. Interfaces*, 2014, **6**, 3594–3599.

98 Y. Ji, C. Y. Zhang, H. J. Niu, X. F. Zhao, C. Wang, C. L. Qin, W. Wang and X. D. Bai, *Dyes Pigm.*, 2016, **125**, 106–115.

99 C. Y. Zhang, Y. J. Hou, H. J. Niu, Y. F. Lian, X. D. Bai, C. Wang and W. Wang, *J. Electroanal. Chem.*, 2014, **717**, 165–171.

100 X. T. Wu, Y. S. Wu, C. Y. Zhang, H. J. Niu, L. Lei, C. L. Qin, C. Wang, X. D. Bai and W. Wang, *RSC Adv.*, 2015, **5**, 58843–58853.

101 H.-J. Yen and G.-S. Liou, *Org. Electron.*, 2010, **11**, 299–310.

102 L. Sicard, D. Navarathne, T. Skalski and W. G. Skene, *Adv. Funct. Mater.*, 2013, **23**, 3549–3559.

103 H. J. Niu, J. W. Cai, P. Zhao, C. Wang, X. D. Bai and W. Wang, *Dyes Pigm.*, 2013, **96**, 158–169.

104 X. C. Ma, H. J. Niu, H. L. Wen, S. H. Wang, Y. F. Lian, X. K. Jiang, C. Wang, X. D. Bai and W. Wang, *J. Mater. Chem. C*, 2015, **3**, 3482–3493.

105 X. Ma, Y. S. Wu, H. L. Wen, H. J. Niu, C. Wang, C. L. Qin, X. D. Bai, L. Lei and W. Wang, *RSC Adv.*, 2016, **6**, 4564–4575.

106 L. C. Lin, H. J. Yen, C. J. Chen, C. L. Tsai and G. S. Liou, *Chem. Commun.*, 2014, **50**, 13917–13920.

107 L. Hao, W. Wang, H. Niu and Y. Zhou, *Electrochim. Acta*, 2017, **246**, 259–268.

108 O. I. Negru, L. Vacareanu and M. Grigoras, *eXPRESS Polym. Lett.*, 2014, **8**, 647–658.

109 M. L. Keshtov, Y. A. Udum, L. Toppare, V. S. Kochurov and A. R. Khokhlov, *Mater. Chem. Phys.*, 2013, **139**, 936–943.

110 W. Kaim and G. K. Lahiri, *Angew. Chem., Int. Ed.*, 2007, **46**, 1778–1796.

111 J.-H. Tang, C.-J. Yao, B.-B. Cui and Y.-W. Zhong, *Chem. Rec.*, 2016, **16**, 754–767.

112 P. Mondal, M. Chatterjee, A. Paretzki, K. Beyer, W. Kaim and G. K. Lahiri, *Inorg. Chem.*, 2016, **55**, 3105–3116.

113 G. de Ruiter, L. Motiei, J. Choudhury, N. Oded and M. E. van der Boom, *Angew. Chem.*, 2010, **122**, 4890–4893.

114 C. Simão, M. Mas-Torrent, J. Casado-Montenegro, F. Otón, J. Veciana and C. Rovira, *J. Am. Chem. Soc.*, 2011, **133**, 13256–13259.

115 G. de Ruiter and M. E. van der Boom, *Acc. Chem. Res.*, 2011, **44**, 563–573.

116 M. Mas-Torrent, C. Rovira and J. Veciana, *Adv. Mater.*, 2013, **25**, 462–468.

117 A. Winter, S. Hoeppener, G. R. Newkome and U. S. Schubert, *Adv. Mater.*, 2011, **23**, 3484–3498.

118 J. Poppenberg, S. Richter, C. H. H. Traulsen, E. Darlatt, B. Baytekin, T. Heinrich, P. M. Deutinger, K. Huth, W. E. S. Unger and C. A. Schalley, *Chem. Sci.*, 2013, **4**, 3131–3139.

119 T. Nagashima, H. Ozawa, T. Suzuki, T. Nakabayashi, K. Kanaizuka and M.-A. Haga, *Chem. – Eur. J.*, 2016, **22**, 1658–1667.

120 C.-J. Yao, Y.-W. Zhong, H.-J. Nie, H. D. Abruña and J. Yao, *J. Am. Chem. Soc.*, 2011, **133**, 20720–20723.

121 Y.-W. Zhong, Z.-L. Gong, J.-Y. Shao and J. Yao, *Coord. Chem. Rev.*, 2016, **312**, 22–40.

122 W. Polit, T. Exner, E. Wuttke and F. Winter Rainer, *BioInorg. React. Mech.*, 2012, **8**, 85–105.

123 J.-J. Shen and Y.-W. Zhong, *Sci. Rep.*, 2015, **5**, 13835.

124 G. Grelaud, M. P. Cifuentes, T. Schwich, G. Argouarch, S. Petrie, R. Stranger, F. Paul and M. G. Humphrey, *Eur. J. Inorg. Chem.*, 2012, **2012**, 65–75.

125 G. Qian and Z. Y. Wang, *Chem. – Asian J.*, 2010, **5**, 1006–1029.

126 W. Kaim, *Coord. Chem. Rev.*, 2011, **255**, 2503–2513.

127 Y. H. Qi, P. Desjardins, X. S. Meng and Z. Y. Wang, *Opt. Mater.*, 2003, **21**, 255–263.

128 C. Friebe, M. D. Hager, A. Winter and U. S. Schubert, *Adv. Mater.*, 2012, **24**, 332–345.

129 B. Tieke, *Curr. Opin. Colloid Interface Sci.*, 2011, **16**, 499–507.

130 B. B. Cui, Y. W. Zhong and J. Yao, *J. Am. Chem. Soc.*, 2015, **137**, 4058–4061.

131 J. H. Tang, Y. Q. He, J. Y. Shao, Z. L. Gong and Y. W. Zhong, *Sci. Rep.*, 2016, **6**, 35253.

132 C. B. Fan, C. Q. Ye, X. M. Wang, Z. G. Chen, Y. Y. Zhou, Z. Q. Liang and X. T. Tao, *Macromolecules*, 2015, **48**, 6465–6473.

133 P. Audebert and F. Miomandre, *Chem. Sci.*, 2013, **4**, 575–584.

134 M. Irie, T. Fukaminato, K. Matsuda and S. Kobatake, *Chem. Rev.*, 2014, **114**, 12174–12277.

135 R. J. Mortimer, D. R. Rosseinsky and P. M. S. Monk, *Electrochromic Materials and Devices*, Wiley, 2015.

136 V. Croué, S. Goeb, G. Szalóki, M. Allain and M. Sallé, *Angew. Chem., Int. Ed.*, 2016, **55**, 1746–1750.

137 J. Winsberg, T. Hagemann, T. Janoschka, M. D. Hager and U. S. Schubert, *Angew. Chem., Int. Ed.*, 2017, **56**, 686–711.

138 K. Yazaki, S. Noda, Y. Tanaka, Y. Sei, M. Akita and M. Yoshizawa, *Angew. Chem., Int. Ed.*, 2016, **55**, 15031–15034.

139 C. R. Benson, E. M. Fatila, S. Lee, M. G. Marzo, M. Pink, M. B. Mills, K. E. Preuss and A. H. Flood, *J. Am. Chem. Soc.*, 2016, **138**, 15057–15065.

140 Q. Chen, J. Sun, P. Li, I. Hod, P. Z. Moghadam, Z. S. Kean, R. Q. Snurr, J. T. Hupp, O. K. Farha and J. F. Stoddart, *J. Am. Chem. Soc.*, 2016, **138**, 14242–14245.

141 J. Schäfer, M. Holzapfel, B. Mladenova, D. Kattnig, I. Krummenacher, H. Braunschweig, G. Grampp and C. Lambert, *J. Am. Chem. Soc.*, 2017, **139**, 6200–6209.

142 J. R. Jennings, W. Y. Lim, S. M. Zakeeruddin, M. Gratzel and Q. Wang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 2827–2832.

143 J. Nagasaki, S. Hiroto and H. Shinokubo, *Chem. – Asian J.*, 2017, **12**, 2311–2317.

144 Y. Li, T. Tan, S. Wang, Y. Xiao and X. Li, *Dyes Pigm.*, 2017, **144**, 262–270.

145 C. Quinton, V. Alain-Rizzo, C. Dumas-Verdes, F. Miomandre, G. Clavier and P. Audebert, *Chem. – Eur. J.*, 2015, **21**, 2230–2240.

146 H. Y. Jin, X. G. Li, T. F. Tan, S. R. Wang, Y. Xiao and J. H. Tian, *Dyes Pigm.*, 2014, **106**, 154–160.

147 F. Chen, X. Fu, J. Zhang and X. Wan, *Electrochim. Acta*, 2013, **99**, 211–218.

148 X. T. Wu, W. Wang, B. Li, Y. J. Hou, H. J. Niu, Y. H. Zhang, S. H. Wang and X. D. Bai, *Spectrochim. Acta, Part A*, 2015, **140**, 398–406.

149 H. L. Wen, H. J. Niu, B. Li, X. C. Ma, X. D. Bai, Y. H. Zhang and W. Wang, *Synth. Met.*, 2015, **202**, 89–97.

150 Y. Li, Y. H. Zhang, H. J. Niu, C. Wang, C. L. Qin, X. D. Bai and W. Wang, *New J. Chem.*, 2016, **40**, 5245–5254.

151 K. B. Vincent, M. Parthey, D. S. Yufit, M. Kaupp and P. J. Low, *Polyhedron*, 2015, **86**, 31–42.