



# Design and preparation of triphenylamine-based polymeric materials towards emergent optoelectronic applications



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## ABSTRACT

This comprehensive review describes the recent development of triphenylamine-based advanced materials for various optoelectronic applications, such as electrochromic, electrofluorochromic, and polymeric memory devices. We herein systemically discuss the structural design, optical and electrical properties of different triphenylamine-containing high-performance polymers that will be beneficial for polymer chemists and scientific community to have deeper and broader understanding of the recent developments and further prompt the engineering and conceptual design of materials for a number of emerging applications (data storage, displays, and flexible electronics). Finally, perspectives on applications beyond the state-of-the-art are also included.

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## Contents

1. Introduction .....	251
2. Triphenylamine-based electrochromic materials .....	253
2.1. TPA-based small molecules .....	253
2.2. Intervalence charge transfer across bridged-TPAs .....	253
2.3. TPA-based electrochromic HPPs .....	254
2.3.1. Polyimides .....	254
2.3.2. Polyamides .....	255
2.3.3. Poly(amide-imide)s .....	256
2.3.4. Poly(ether-imide)s and Poly(ether-amide)s .....	256
2.3.5. Poly(hydrazide)s and Poly(oxadiazole)s .....	257
2.3.6. Poly(triphenylamine)s .....	257
2.4. Other TPA-based polymers .....	260
2.4.1. Conjugate polymers .....	260

**Abbreviations:** 6FDA, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride; A, acceptor; arylamine, aromatic amine; BTI, benzenetetracarboxydiimide; CT, charge transfer; D, donor; DRAM, dynamic random access memory; DSDA, 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride; EC, electrochromic; EFC, electrofluorochromism; ET, electron-transfer; Fc, ferrocene; HOMO, highest occupied molecular orbital; HPP, high-performance polymer; HV, heptyl viologen; ITO, indium tin oxide; LUMO, lowest unoccupied molecular orbital; MV, mixed-valence; NA, 1,8-naphthalic anhydride; NIR, near-infrared; NPDA, 1,4,5,8-naphthalenetetracarboxylic dianhydride; NTI, naphthalenetetracarboxydiimide; ODPDA, oxydiphthalic dianhydride; OHTPA, hydroxyl-triphenylamine; PA, polyamide; PC<sub>61</sub>BM, [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester; PEA, 3,4-perylene-dicarboxylic anhydride; PET, photoinduced electron transfer; PI, polyimide; PL, photoluminescence; PMDA, pyromellitic dianhydride; polyarylate, aromatic polyester; PTA, phthalic anhydride; PTI, perylenetetracarboxydiimide; RRAM, resistive random access memory; SCLC, space charge-limited current; SRAM, static random access memory; TPA, triphenylamine; TPB, tetraphenylbenzidine; TPPA, tetraphenyl-*p*-phenylenediamine; WORM, write-once read-many times.

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2.4.2.	Epoxy	260
2.4.3.	Polyurethane	260
2.4.4.	Poly(azomethine)	261
2.4.5.	Poly(benzoxazine)	262
2.4.6.	Polyester	262
3.	Triphenylamine-based resistive switching polymeric memory devices	263
3.1.	Mechanism	263
3.1.1.	Charge transfer	263
3.1.2.	Space charge traps	264
3.1.3.	Filament conduction	265
3.2.	HPPs for volatile memory devices	265
3.2.1.	DRAM properties	265
3.2.2.	SRAM properties	265
3.3.	HPPs for non-volatile memory devices	267
3.3.1.	WORM properties	267
3.3.2.	Flash properties	267
3.4.	Molecular design on volatility	269
3.4.1.	Donor effect	269
3.4.2.	Acceptor effect	270
3.4.3.	Linkage effect	271
3.4.4.	Compositional effect	274
3.4.5.	Thickness effect	274
3.4.6.	HPP/PC <sub>61</sub> BM hybrids	275
3.5.	Flexible HPP electrical memory devices	275
4.	Triphenylamine-based materials for electrofluorochromic devices	275
4.1.	Principle/Mechanism	275
4.2.	Electroswitchable fluorophores	276
4.2.1.	Small molecules	276
4.2.2.	Polymer materials	278
5.	Conclusions and outlook	280
	Acknowledgements	281
	References	281

## 1. Introduction

Triphenylamine (TPA), a propeller-shaped molecule exhibits good thermal and morphological stability, leading to emergent optoelectronic properties and potential applications. Importantly, the high oxidizability, interesting electroactive, and photoactive properties of TPA combined with the high stability of the corresponding radical cation make it a very good hole transporting species [1]. Therefore, TPA-based derivatives or polymers are widely used as photoconductors, light-emitters [2], electrochromics [3], and especially hole transporting materials in organic light-emitting diodes, solar cells, organic field-effect transistors and photorefractive materials [4–8].

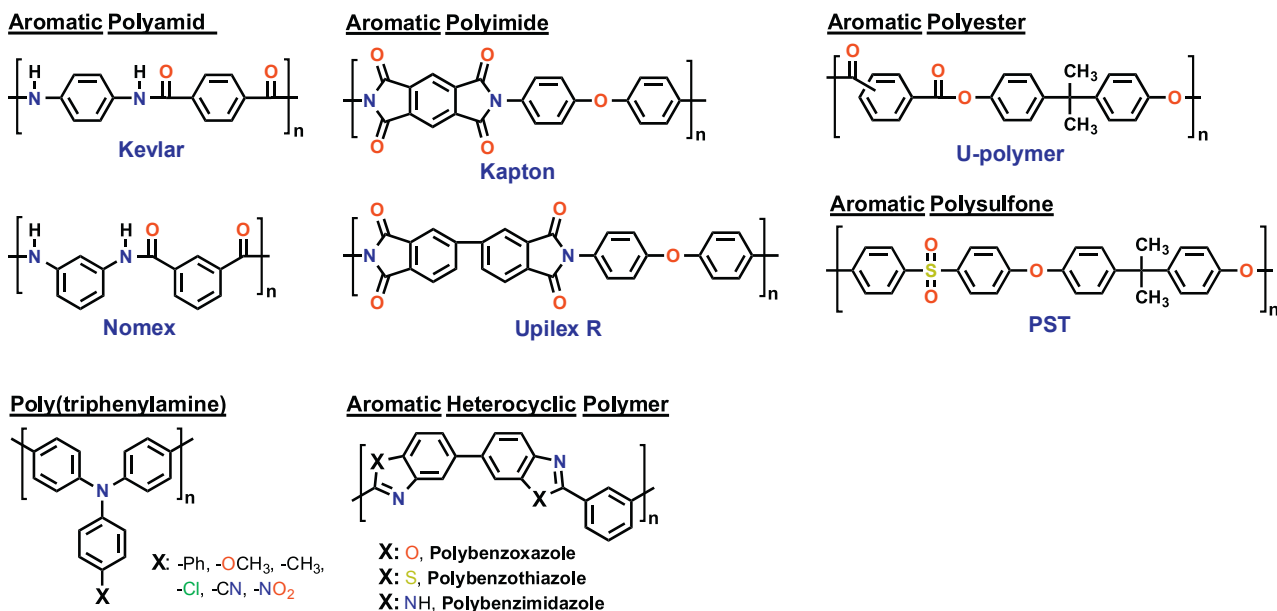
As elaborated in the following, incorporating TPA into polymer backbone enhances the processing of high-performance polymers (HPPs). HPPs are major and desirable synthetic materials of the 21st century. The synthesis and development of HPPs has received extensive attention from many polymer chemists and physicists in the past three decades. Mostly, HPPs exhibit outstanding dimensional stability and chemical stability under extreme operation condition. Hill and Walker initiated the HPPs by incorporating aromatic compositions into polymer chains, resulting in a notable thermal stability enhancement [9]. For this reason, considerable research has been directed toward aromatic compositions. Therefore, HPPs, which tend to include more aromatic moieties in their structure, have been in high demand since the late 1950s in order to meet the needs of aerospace, military, electronics, and many industrial applications. Several aromatic HPPs have reached commercialization, including aromatic polyimides (PIs), polyamides (PAs), polyTPA, polysulfones, polyesters, and heterocyclic polymers (Scheme 1). Aromatic PA and PI, such as DuPont's Kevlar fiber and Kapton film, respectively, have been well developed

and continuously draw greater interest than other HPPs due to their high mechanical strength, low flammability, excellent oxidative and thermal stability, good radiation and chemical resistance [10–21].

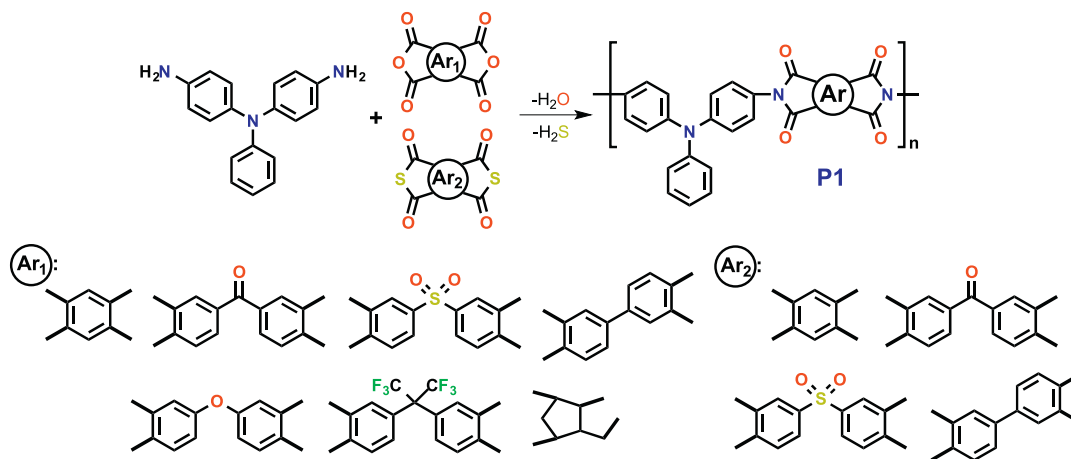
The high rigidity of the backbone and strong intermolecular interactions result in high glass-transition or melting temperatures and low solubility in organic solvents [20,22]. These features make them extremely difficult to process and limit their technological and practical applications. The incorporation of bulky TPA groups into the polymer structure offers a method to overcome such restrictions without decreasing thermal stability [23–31]. Since the bulky and propeller-shaped TPA structure incorporated into the polymer backbone tends to be packing-disruptive, most of the prepared HPPs are amorphous, with high thermal stability, good film-forming capability, and good solubility [32–34].

Among the HPPs, aromatic PIs have been considered as significant materials in many industrial applications, especially in the electric packaging and semiconductor industry. The outstanding and desirable characteristics of aromatic PIs come from their rigid backbones and strong intramolecular and intermolecular forces within the polymer chains. The first TPA-based PIs **P1** prepared from 4,4'-diaminoTPA and various tetracarboxylic dianhydrides were first reported in 1991 (Scheme 2) [35–37]. These thermally stable polymers showed high solubility in many polar solvents and exhibited high glass-transition temperatures and high char yields.

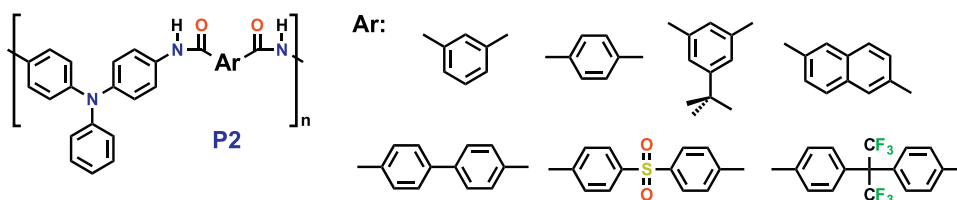
It is also well known that the microelectronic materials, aromatic PAs, have attracted numerous interests due to their thermal and mechanical resistance. Similar to PIs, incorporation of packing-disruptive TPA units not only preserves thermal stability and glass transition temperature, but enhances the solubility and facilitates the film-forming ability, which is beneficial for their fabrication of large-area, thin-film optoelectronic devices. The first PAs **P2** based



Scheme 1. Commercialized high-performance polymers and poly(triphenylamine)s.



Scheme 2. Reaction scheme of the first TPA-based polyimides.



Scheme 3. Reaction scheme of the first TPA-based polyamides.

on TPA groups were synthesized from 4,4'-diaminoTPA and various dicarboxylic acids by Imai et al. in 1990 (Scheme 3) [38].

In addition to the PIs and PAs prepared by polycondensation reaction, polymeric TPAs could also be prepared by using Grignard [39] and palladium coupling reactions (Scheme 1) [40]. However, these synthetic approaches require multiple steps to prepare the corresponding monomers. Therefore, a facile approach, oxidative coupling polymerization, was utilized to replace the aforementioned reaction. The oxidative coupling polymerization could be carried out for preparing a series of different *para*-substituted TPA-

based polymers with high molecular weight by using an oxidant FeCl<sub>3</sub> [41,42]. These results also showed that the incorporation of electron-withdrawing substituents provides an increased molecular weight, good thermal stability, adjustable band gaps, and good electrochemical stability. In this review, the recent developments of TPA-based advanced materials have been summarized, with an emphasis on the synthetic approaches for preparing the polymers as well as their potential applications, such as electrochromic, electrofluorochromic, and polymeric memory devices (Fig. 1).



**Fig. 1.** Optoelectronic applications of TPA-based technology. TPA-based materials have increasingly found applications in a wide range of areas, such as data storage, electrochromic, and electrofluorochromic devices.

## 2. Triphenylamine-based electrochromic materials

### 2.1. TPA-based small molecules

Basically, aromatic amines (arylamines) are colorless unless they have CT interactions with the electronic acceptor species, and could be expected as promising materials in virtue of their plentiful electrochromic (EC) properties. Arylamines emerge a noteworthy color in an organic solution when a form of radical-cation shows up due to the mono-electron oxidation. The nitrogen center of triarylamine is rich in electrons, and can be easily oxidized to give birth to a radical cation form accompanied with an outstanding color change. Consequently, research on the synthesis and EC properties of polymer incorporated with the triarylamine unit has gradually drawn attentions and been issued in publications [43–45].

Although several categorized materials show EC behavior, only those with proper EC performance parameters [46,47] could be potentially applicable in practical EC devices. EC anti-glare car rearview mirrors have already been successfully commercialized, with other promising EC materials including their applications in light-transmission or controllable light-reflective devices for optical

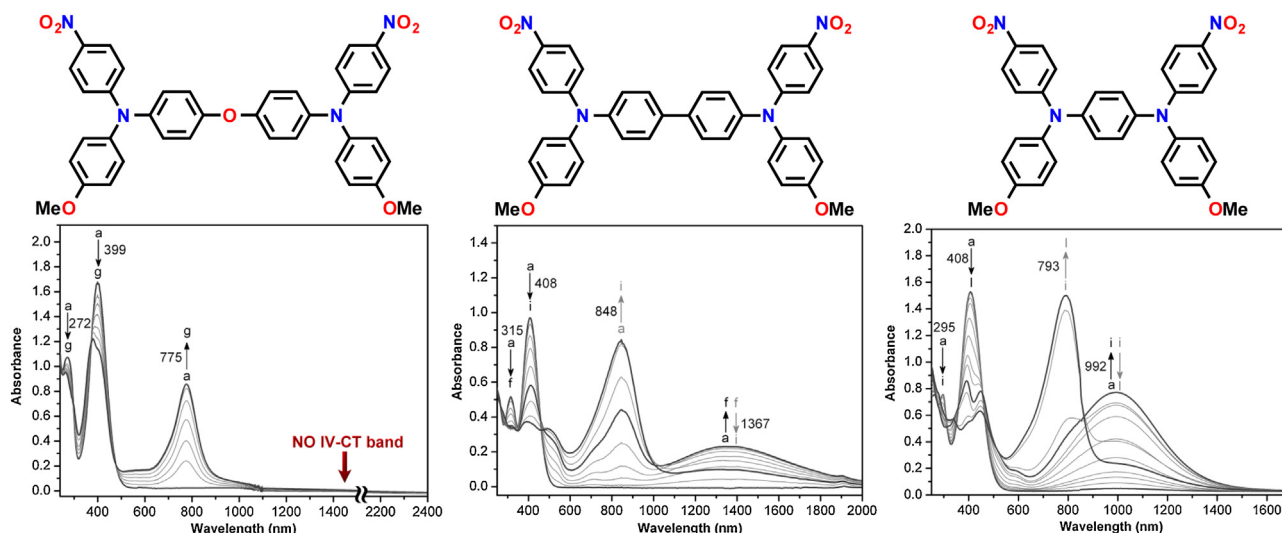
storage and information, sunglasses, protective camouflage eye-wear for the military, aircraft and vehicle canopies, glare-reduction systems for offices, and ‘smart windows’ for use in buildings and cars [46]. With that, EC panoramic rearview mirrors for vehicles have already reached commercial consideration. For the safety issue, the ‘after image’ to stay on the eye’s retina from the operation of mirror-reflected glare should be prevented. Therefore, EC materials with a high contrast ratio, coloration efficiency (absorbance change/charge injected per unit area), and cycle life are highly in demand. Smart windows fabricated by EC materials can tolerate response times of up to minutes even the displays usually need fast response times. Basically, EC materials with potentials for practical applications should possess the following criteria:

- (1) Low driving voltage
- (2) Rapid response time (second of mirror to minute of window)
- (3) High color contrast (transmittance attenuation =  $\Delta T > 30\%$ )
- (4) Long cycle life (>10 yr for window, >3 yr for mirror)
- (5) Environmental stability (electrochemical, thermal, & UV)
- (6) Low cost, easy processing
- (7) Multiple colors with the same material

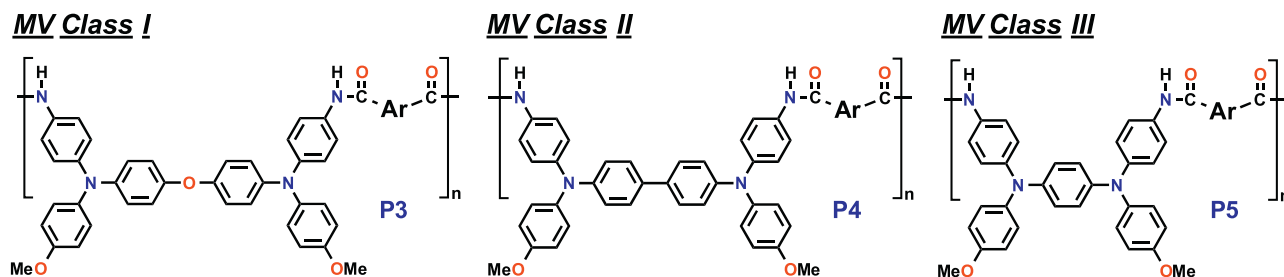
Therefore, the main aim of this section is to provide a comprehensive overview and to cover a majority of the works in the recent decade regarding arylamine-based EC HPPs and to demonstrate how the structural design influences the corresponding EC properties.

### 2.2. Intervalence charge transfer across bridged-TPAs

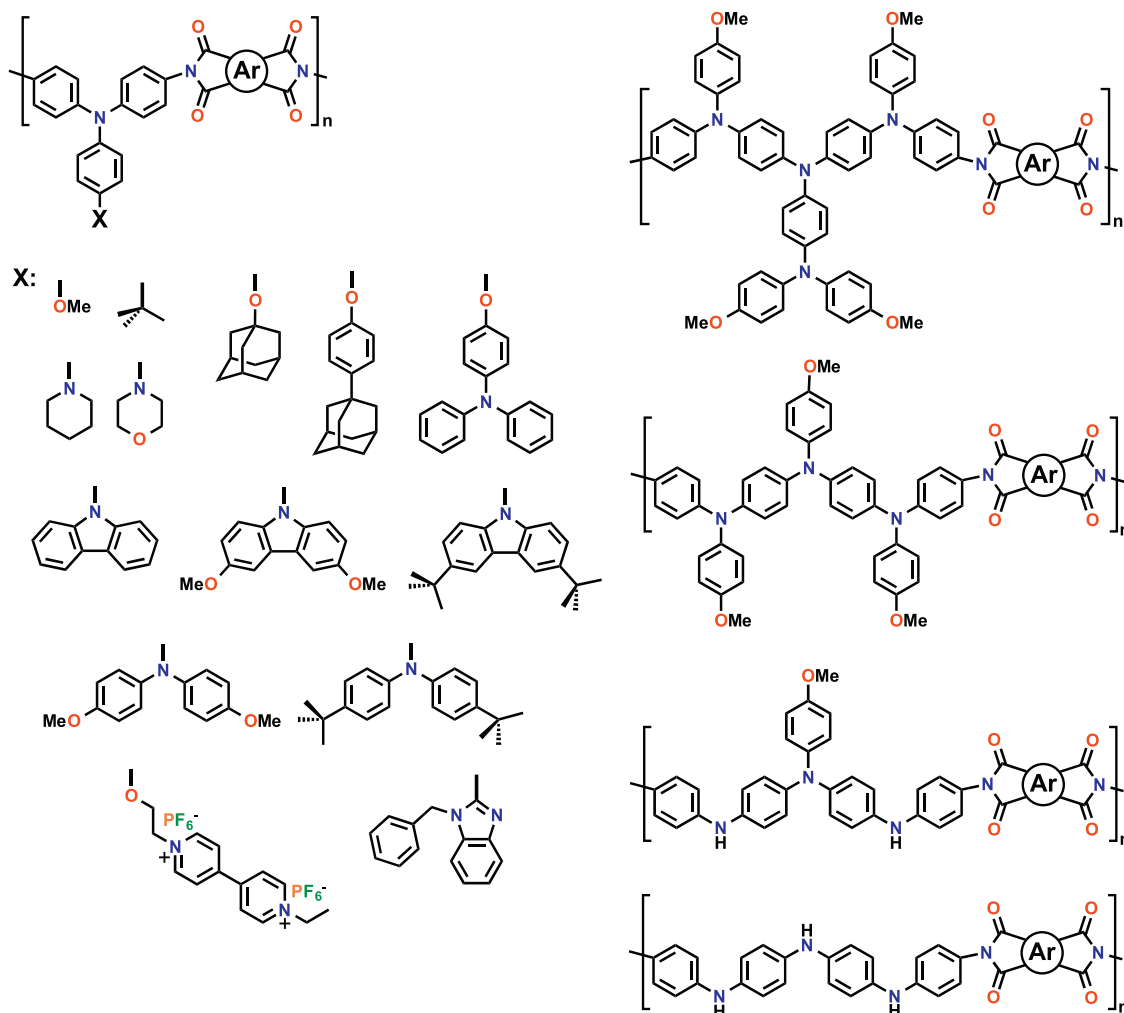
Electron-transfer (ET) interaction is one of the most fundamental processes between electroactive species for chemists [48] and biologists [49]. Creutz and Taube [50,51] initiated the basic aspects of ET theories and check the applicability of Hush theory for interpreting intervalence charge-transfer (CT) [52,53] by using mixed-valence (MV) inorganic derivatives as model systems. In 1968, Robin and Day [54] categorized MV compounds containing two (or more) redox centers into three types: (class I) separate entities are performed by the completely localized redox centers, (class II) intermediate coupling between the MV centers exists, and (class III) complete delocalization could be observed due to the strong coupling.



**Fig. 2.** Absorption spectral change of representative compounds with MV class I-III at various applied potential. [43], Copyright 2011. Reproduced with permission from the Royal Society of Chemistry.



Scheme 4. The representative scheme of the bridged aryldiamines with MV I/II/III transitions.



Scheme 5. TPA-based high-performance polyimides.

Therefore, the tetraphenyl-*p*-phenylenediamine (TPPA) cation radical and tetraphenylbenzidine (TPB) cation radical, reported respectively as a symmetrical delocalized class III structure and class II structure, both lead intervalence CT absorption bands in the near-infrared (NIR) region (Fig. 2) [55–57]. As a result, the aryldiamine-based derivatives are considered as interesting anodic EC materials for NIR applications. Recently, our group has systematically developed TPPA-based PA **P5** [58] and TPB-based PA **P4** [59], which exhibited traditional MV class III and II transition, respectively. Furthermore, the electroactive polymers bridged by ether-linkage can be characterized as MV class I due to the completely isolated two redox centers (Scheme 4) [60]. By introducing ether-linkage into bis(TPA)ether unit, the resulting polymers **P3** containing two separated redox centers exhibited independent

electrochemical behavior, showing that the two electrons within bis(TPA)ether moiety are removed simultaneously to form two radical cations without intramolecular ET. The electrochemistry and MV I/II/III transition of the corresponding materials with various N–N distances were synthesized and investigated for the bridged triarylamine system to perform the different intramolecular ET capability.

### 2.3. TPA-based electrochromic HPPs

#### 2.3.1. Polyimides

In 2005, our group first disclosed interesting EC properties of aromatic polyimides containing TPA groups from a newly synthesized diamine, *N,N*-bis(4-aminophenyl)-*N',N'*-diphenyl-1,4-



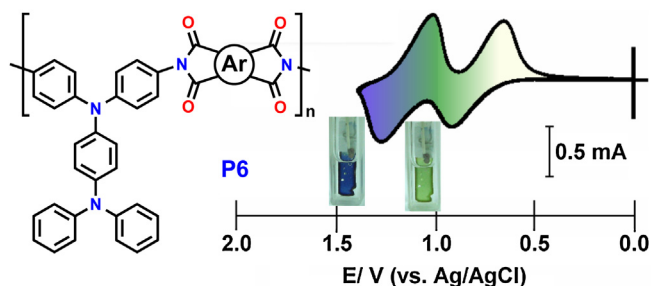


Fig. 3. Cyclic voltammograms of first EC PI and its EC behavior. [60], Copyright 2005. Reproduced with permission from the American Chemical Society.

phenylenediamine, and various tetracarboxylic dianhydrides by polycondensation reactions (Fig. 3) [61]. Some of the PIs revealed moderate solubility in several organic solvents, which can be further solution cast into flexible, tough, and transparent films. The thermally stable PI films exhibited two well-defined oxidation redox couples (at 0.78 and 1.14 V versus Ag/AgCl) with distinct color changes from pale yellowish to green and then blue during oxidative scanning.

In the following years, Liou and Hsiao groups constantly reported the synthesis of high-performance PIs based on TPA or other electroactive triarylamine derivatives as electroactive functional moieties (Scheme 5) [62–73]. Most of the PIs were

organo-processable and thermally stable with excellent adhesion with indium tin oxide (ITO)-coated glass electrode and good electrochemical stability. The TPA-based PIs also revealed EC characteristics when scanning potentials positively and are considered as great anodic EC materials due to proper oxidation potentials, electrochemical stability, and thin film formability [74–78].

Another ambipolar PI with starburst triarylamine unit exhibited high contrast ratio and electroactive stability during EC operation with multi-colors at different applied potentials due to its four oxidation and two reduction states (Fig. 4). The film colors are distributed homogeneously across the polymer film and reveal excellent stability for several thousands of redox cycles. The PI shows good contrast both in the visible and NIR regions, with an extremely high optical transmittance change of 82% at 1010 nm for purple coloring at the second oxidation stage, and 80% at 735 nm for the bluish-green coloring at the fourth oxidation stage. In addition, when the potential was switched between 0 and 0.60 V, the PI thin film revealed a switching time of 3.99 s for the coloring process and 0.90 s for bleaching. When the switched potential was set between 0 and 0.90 V, the PI thin film required 3.12 s for coloration and 1.74 s for bleaching.

### 2.3.2. Polyamides

Since 2005, Liou, Hsiao [6,62,65–67,79–97], and other groups [77,98–103] also developed numerous TPA-based EC PAs with extensive color transitions (Scheme 6). Similarly, these organosol-

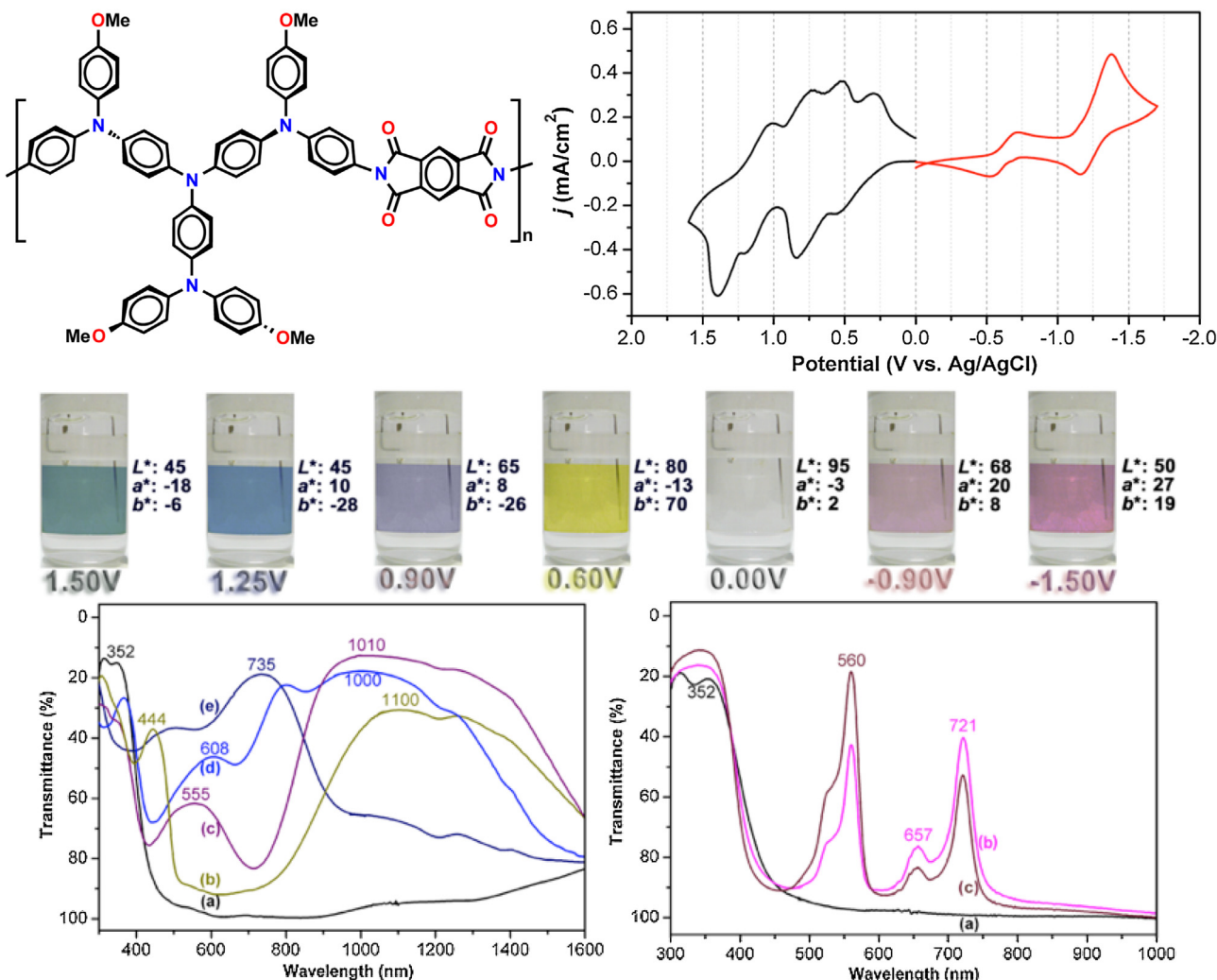
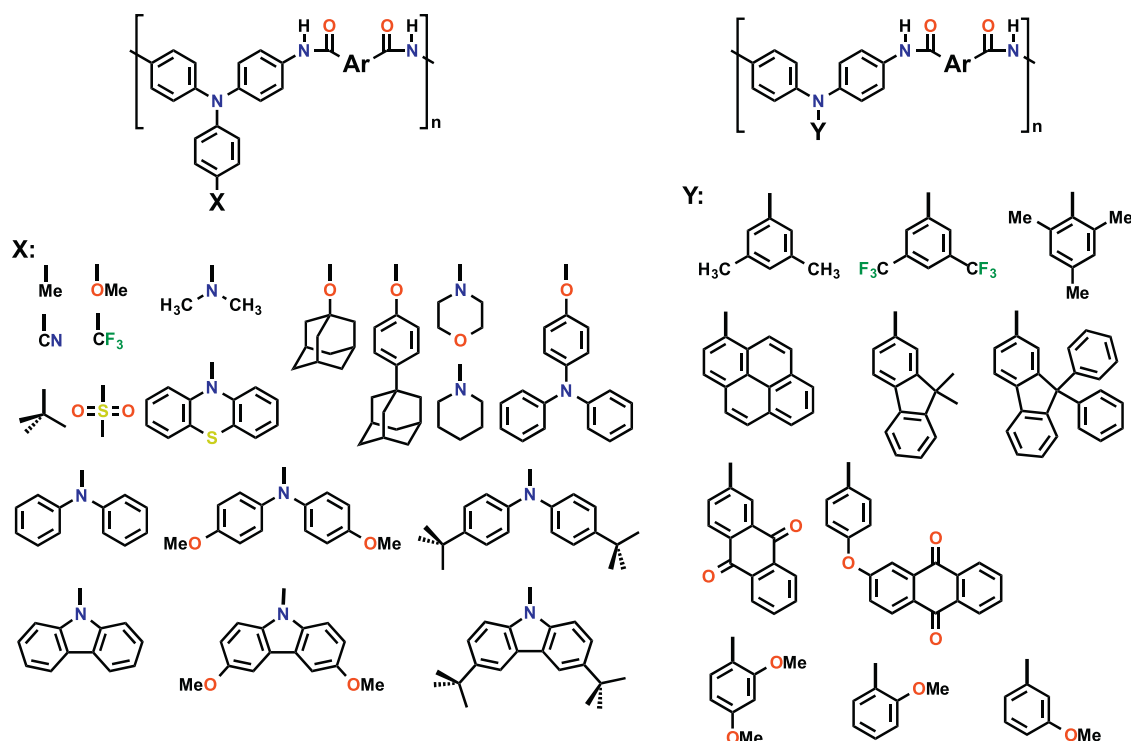


Fig. 4. Cyclic voltammograms of the starburst EC PI and its EC behavior. [204], Copyright 2013. Reproduced with permission from the Royal Society of Chemistry.



Scheme 6. TPA-based high-performance polyamides.

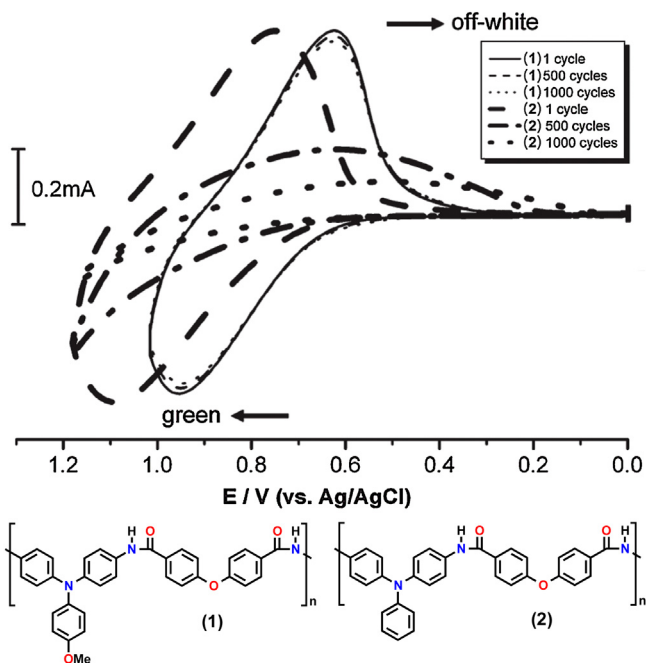


Fig. 5. Cyclic voltammograms of PAs (1) and (2) films over 1000 cyclic scans. [80], Copyright 2007. Reproduced with permission from the Royal Society of Chemistry.

uble polymers showed high levels of thermal stability and high glass-transition temperatures as well as high char yields. Some of the PA thin films revealed reversible electrochemistry with EC high contrast ratio in the visible range or NIR region, high coloration efficiency, low switching time, and the high stability for long-term EC operation.

The anodically EC PA(1) shown in Fig. 5 exhibited excellent reversible EC stability with good green coloration efficiency and high contrast of optical transmittance change up to 85%. After over

1000 cyclic switches, the polymer films still exhibited excellent reversibility of EC characteristics compared to PA(2) due to the *para*-substituted methoxy groups.

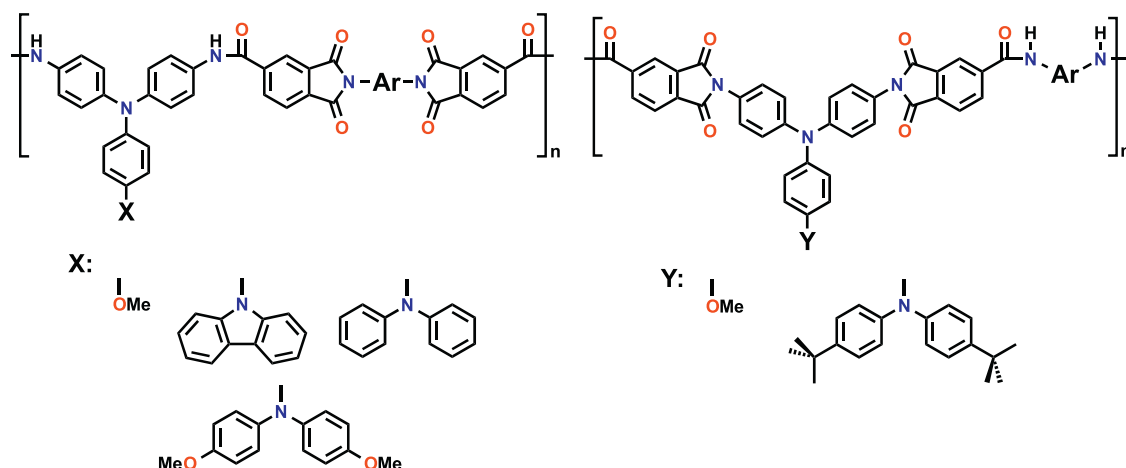
### 2.3.3. Poly(amide-imide)s

The intractable property of aromatic PIs is a critical problem for optoelectronic applications. Copolymerization is an effective approach to overcome this drawback. Poly(amide-imide)s have been developed as alternative materials offering a useful compromise between excellent processability and thermal stability.

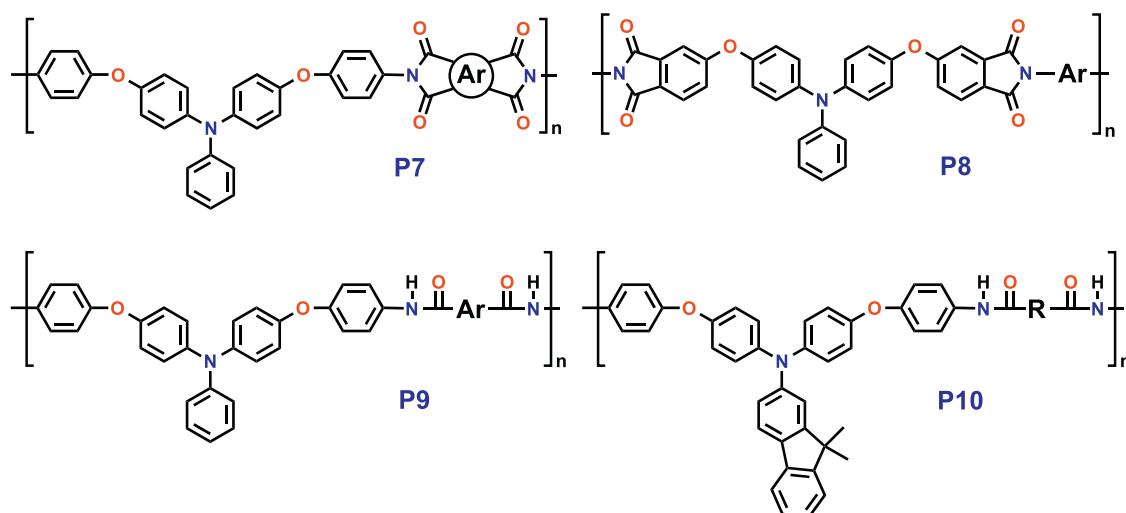
To solve this problem, we also synthesized aromatic poly(amide-imide)s with *para*-methoxy or *para*-*tert*-butyl substituents by the phosphorylation polyamidation (Scheme 7) [104–109]. All the polymers revealed high solubility in polar organic solvents and can be solution cast as flexible, tough, amorphous films. Moreover, these films showed reversible electrochemical oxidation redox couples with good EC stability and high contrast of optical transmittance change.

### 2.3.4. Poly(ether-imide)s and Poly(ether-amide)s

Hsiao [110,111] reported several types of TPA-based solution processable high-performance poly(ether-imide)s **P7** and **P8** derived from TPA-containing bis(ether-anhydride) and bis(*p*-aminophenoxy) monomers, respectively (Scheme 8). On the other hand, poly(ether-amide)s **P9** and **P10** were also prepared from bis(*p*-aminophenoxy)triarylamine via the phosphorylation technique and exhibited good solubility in many organic solvents [112,113]. The good solubility of these poly(ether-imide)s and poly(ether-amide)s can be attributed to the presence of three-dimensional TPA units, together with the flexible ether linkage along the polymer backbone. In addition to the basic characterizations, the poly(ether-imide) and poly(ether-amide) films revealed excellent electrochemical and EC stability. Moreover, these polymers performed enhanced EC performance and redox-stability, as opposed to derivatives without the phenoxy linkage.



Scheme 7. TPA-based high-performance poly(amide-imide)s.



Scheme 8. TPA-based poly(ether-imide)s and poly(ether-amide)s.

### 2.3.5. Poly(hydrazide)s and Poly(oxadiazole)s

Aromatic poly(oxadiazole)s are a class of chemically and thermally stable heterocyclic polymers [11]. Oxadiazole-based conjugated polymers have been extensively studied and fabricated as emission or electron transport layers in polymer light-emitting diodes [114,115]. The primary reason for this use is the high photoluminescence (PL) quantum yield combined with the advantage of simple processability into flexible and mechanically robust films or thin film layers.

However, infusible and insoluble behavior, as well as the tendency to be brittle, limits the processability of polyoxadiazoles based on aromatic segments. To overcome the limitation of processing, structural modification of polyhydrazides, the precursors of polyoxadiazoles, is attractive. Recently, we have reported the synthesis of soluble aromatic polyhydrazides and polyoxadiazoles containing TPA units in the main chain (Scheme 9) [116–121]. Triarylamines have also attracted considerable interest as hole-transporting materials for use in multilayer organic electroluminescence devices due to their relatively high mobility and their low ionization potentials [122–125]. Thanks to the propeller-shaped and bulky TPA units, the prepared polymers were amorphous, organosoluble, and thermally stable. The feasibility of utilizing spin-coating and ink-jet printing processes for large-area electroluminescence devices and possibilities of various chemical modifications (to improve emission efficiencies and allow pattern-

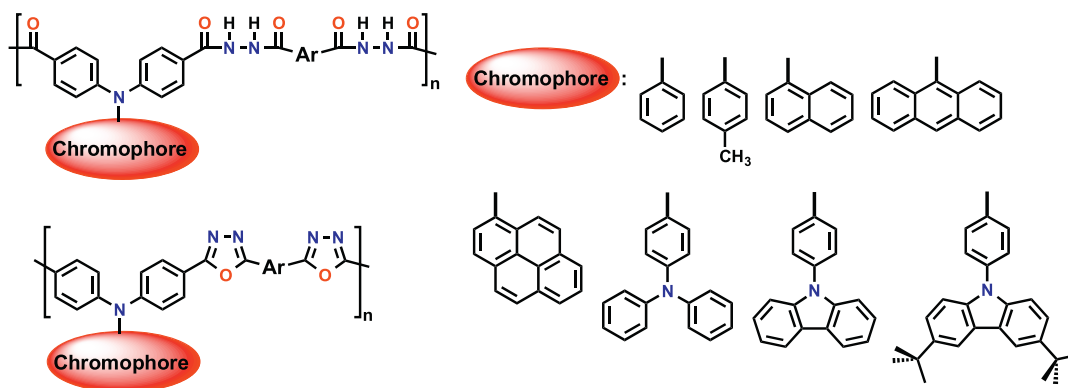
ing) make these triarylamine-containing polymers very attractive [126–130].

### 2.3.6. Poly(triphenylamine)s

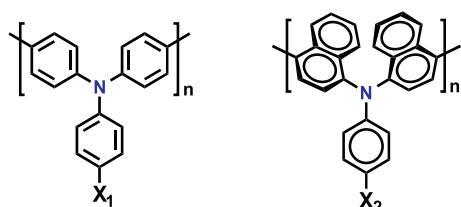
Since the electrical conduction of doped polyaniline was discovered in 1985 [131], research has focused on its applications in lightweight batteries [132,133] and flexible hole-transport layers [134–136]. In particular, polyaniline proved to be a moisture and air stable conductive material, synthesized by simple and inexpensive chemical or electrochemical [137–139] oxidation of aniline [131]. Importantly, a slight modification made to prepare a variety of aniline derivatives afforded the means to optimize and fine-tune the properties of corresponding arylamine polymers. Studies by the Ueda [140] and Buchwald groups [141,142] led to an efficient synthesis of poly(arylamine)s from primary or secondary amines and aryl halides (Scheme 10) [40].

During the past decade, the Liou and Hsiao groups introduced electron-donating species as protecting groups to triarylamine moieties that can prevent the anodic oxidation pathways of the unstable cation radical of TPA<sup>+</sup> to form TPB through tail to tail coupling, reported by Nelson and co-workers [143,144]. Therefore, it is natural to design electropolymerizable monomers by attaching two or more unsubstituted TPA units to an electron-withdrawing core. Indeed, the synthesis of a number of electroactive polymers containing TPA as core fused with thiophene, dithienylpyrrole





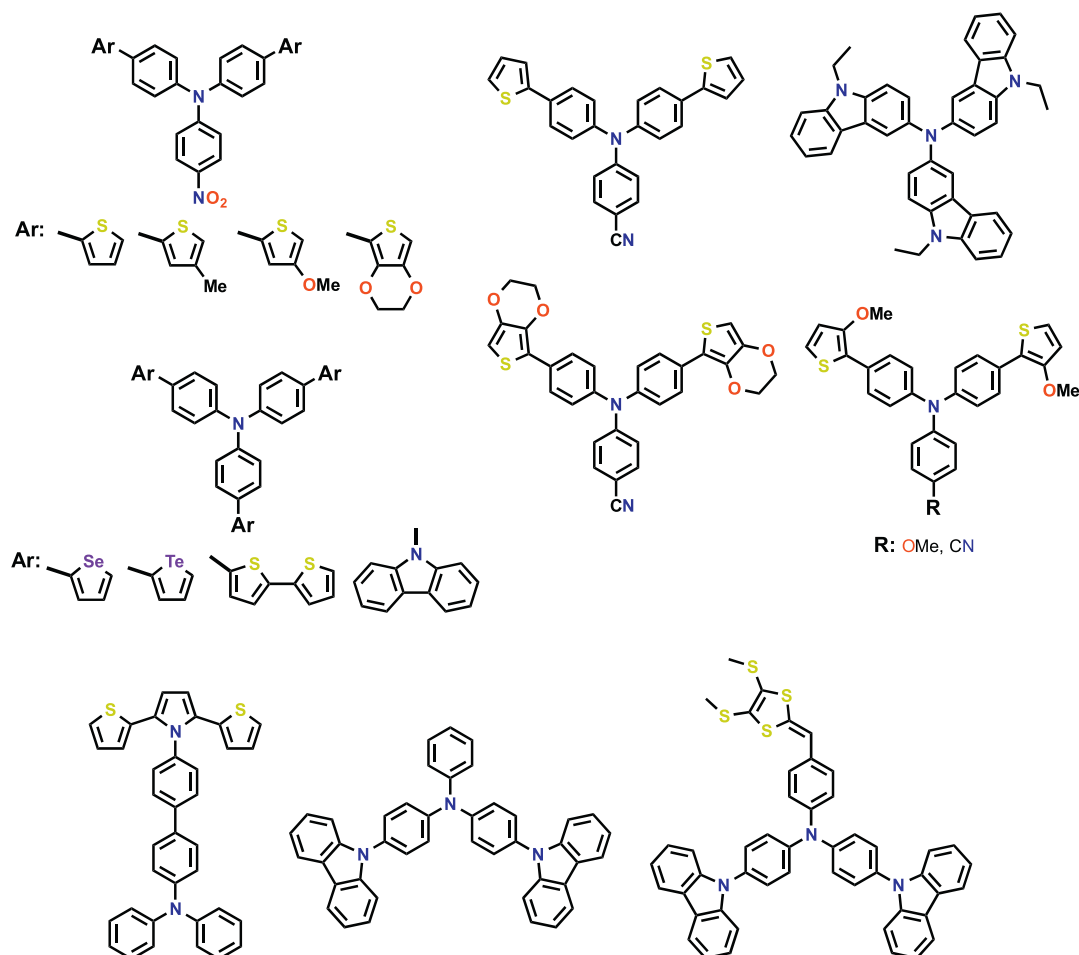
**Scheme 9.** TPA-based poly(hydrazide)s and poly(oxadiazole)s.



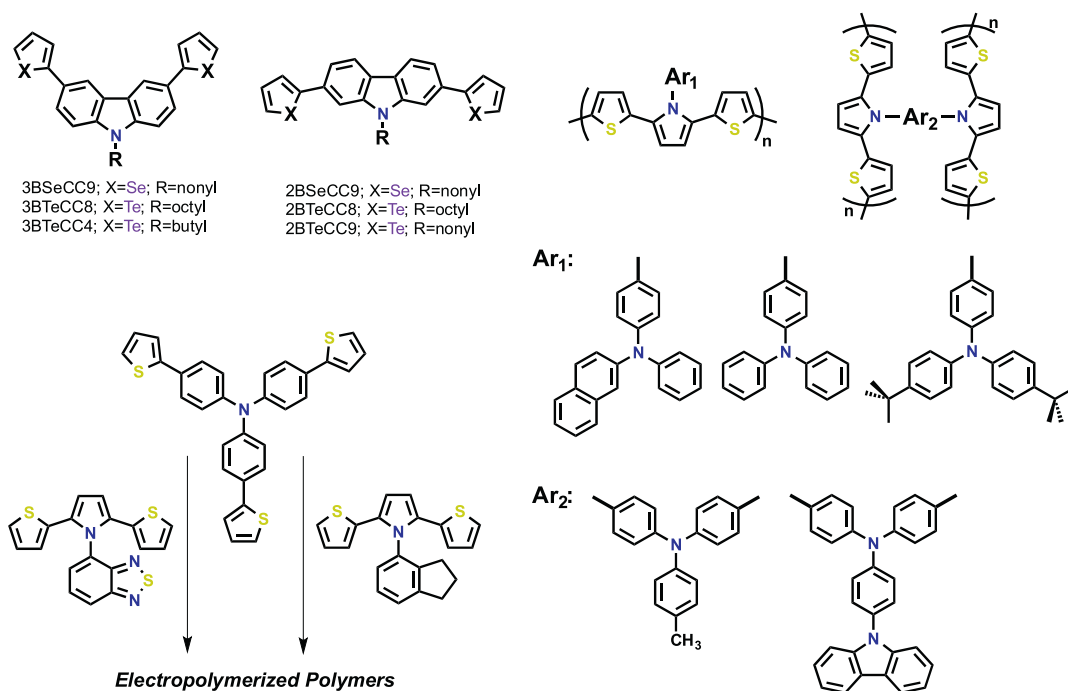
$X_1$  : -Ph, -OMe, -Me, -Cl, -CN, -NO<sub>2</sub>       $X_2$  : -OMe, -Me

**Scheme 10.** Representative scheme of redox-active poly(arylamine)s.

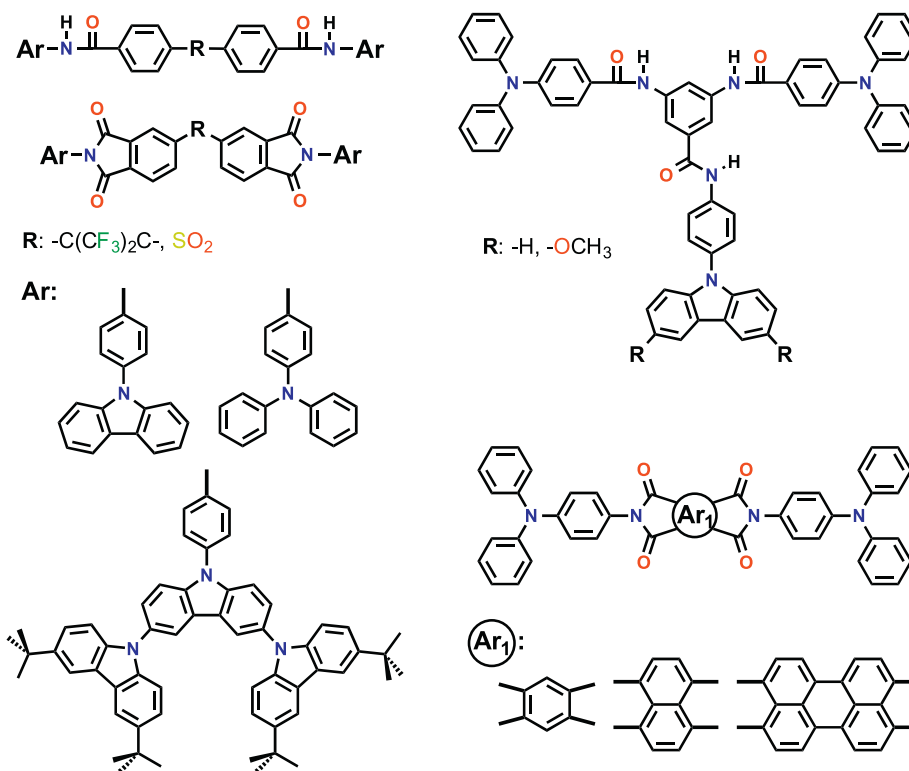
and carbazole derivatives via electropolymerization process has been reported (Schemes 11 and 12) [145–154]. Besides, carbazole is another type of arylamine obtained via dehydrocyclization of diphenylamine at ortho position of diphenyl groups, and can be further substituted or polymerized either at the 3- and 6-positions or 2- and 7-positions using different synthetic strategies and substitution patterns, resulting in high performance materials for optoelectronic applications. On the other hand, the substituent effects of carbazole and *N*-substituted derivatives were first studied systematically by Ambrose and Nelson in 1968 [155]. The *N*-phenylcarbazoles without protecting groups at both the 3 and 6 positions of carbazole ring underwent an initial one-electron



**Scheme 11.** Monomers with TPA electroactive core for electropolymerization.



Scheme 12. Monomers with TPA electroactive core for electropolymerization.



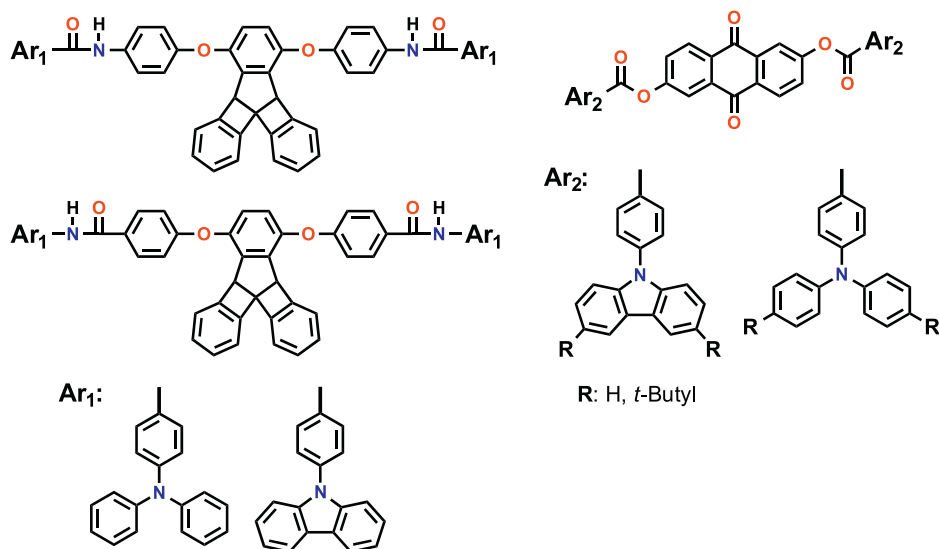
Scheme 13. Several series of TPA and N-phenylcarbazole compounds with amide, imide, and ester linkages for facile electropolymerization.

oxidation to generate a very reactive cation radical; two of these were then coupled at the 3 positions to yield a dimer structure as *N,N'*-diphenyl-3,3'-bicarbazyl. These unprotected TPA and *N*-phenylcarbazole compounds via oxidative dimerization reaction have been employed efficiently combining both a one-step facile synthesis and direct fabrication of electroactive polymer films on an electrode surface. The Hsiao group first reported a series of TPA and *N*-phenylcarbazole compounds with amide, imide and

ester units to obtain polymer films via facile electropolymerization (Scheme 13) [6,156–164].

Besides, amide and imide functional groups may also be used as linkages between TPA and carbazole together with triptycene and anthraquinone groups as new EC polymers (Scheme 14) [165,166].

This procedure significantly shortens the experimental time and avoids the solubility issues often encountered with conventional chemical methods, thus enlarging the scope of candidate



**Scheme 14.** TPA and carbazole together with anthraquinone or triptycene groups for facile electropolymerization.

polymers for EC applications. It is noteworthy that ambipolar polymers with arylamine and imide moieties reveal more interesting multi-color EC behaviors than PA ones upon anodic oxidation and cathodic reduction process. These systematic results provide a model to design triarylamine-based monomers capable to form electrochemically active ambipolar polymers with potential applications in electronic and optoelectronic devices.

#### 2.4. Other TPA-based polymers

##### 2.4.1. Conjugate polymers

Four TPA-based conjugate polymers were synthesized and fabricated as EC devices (Scheme 15) [167]. The authors reported color changes from the neutral to oxidized forms as follows: for **P11a**, orange to dark green; for **P11b**, light yellow to reddish brown; for **P11c**, light blue to grey; and for **P11d**, green to bluish green. Most of the polymers exhibited very good thermal stability as evidenced by less than a 5% weight loss in temperatures exceeding 400 °C.

Skene et al. reported **P12** from a monomer consisting of a benzothiadiazole core flanked by two TPAs and two styrene pendant moieties [168]. The monomer could be immobilized on ITO-coated glass substrates. The resulting 425 nm thick immobilized film was 15% thinner than the monomer coating deposited by spray- and spin-coating. The electroactive film did not delaminate from the electrode upon either washing or cycling electrochemically between its oxidized and neutral states. Its absorption at 460 nm bleached upon electrochemical oxidation with the formation of a strong absorption at 880 nm and in the NIR, similar to the monomer. The perceived reversible color change with applied potential switched between yellow and gray.

Toppare et al. reported a series of benzotriazole and TPA-based random copolymers **P13** and **P14** synthesized via Stille coupling and used to investigate the effect of TPA unit and  $\pi$ -bridges on electrochemical and spectroelectrochemical properties [169]. All polymers showed good solubility and high film quality. Changing  $\pi$ -bridges affect the oxidation potentials significantly due to their electron density on the polymer backbone. TPA unit is definitely a good choice as a potential electron donating and hole transporting material.

##### 2.4.2. Epoxy

Epoxy resin has been considered as a classic material for use in composites, adhesives, and coatings materials due to its advan-

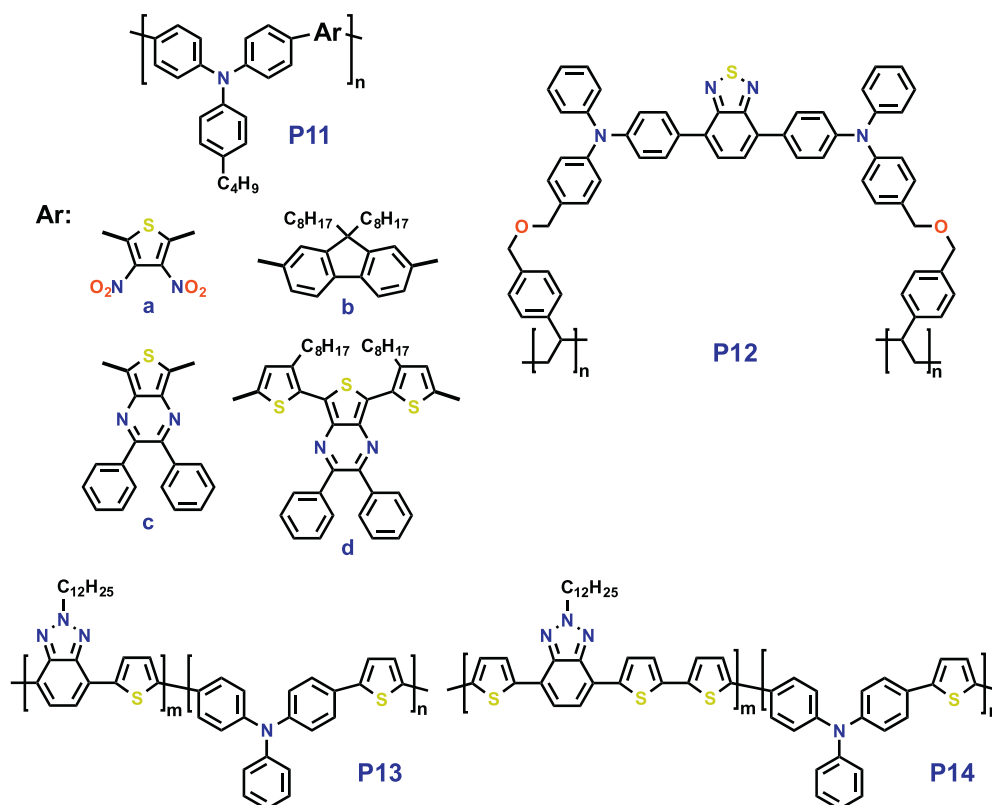
tages, such as low shrinkage, toughness, corrosion resistance, and excellent adhesion [170]. The thermoset epoxy resins with amine, ester, or ether linkages could be obtained by reacting the epoxy groups with hardeners, acids, anhydrides, amines, mercaptans, phenols, or isocyanates. Importantly, TPA groups could be seen as “green hardeners” and could be anticipated to impart flame retardant behavior because they are halogen-free and phosphorus-free with high aromatic content.

Two thermally stable, aliphatic, and anodically EC thermoset epoxy resins were successfully prepared by our group from two TPA-based diamine monomers and aliphatic epoxy triglycidyl isocyanurate via the thermal curing reaction (Scheme 16) [171]. The multi-EC and electrochemically stable TPA-based epoxy materials exhibit high EC contrast in both the visible and NIR regions. Moreover, these transparent TPA-based thermoset epoxy materials with transmittance up to 92.2% at 400 nm in thinfilms could be considered as colorless for many applications. In addition, these TPA-based epoxy resins exhibited much lower oxidative potentials than the corresponding PAs derived from the same TPA-based diamines that can both effectively enhance EC stability and decrease the energy required for practical EC applications.

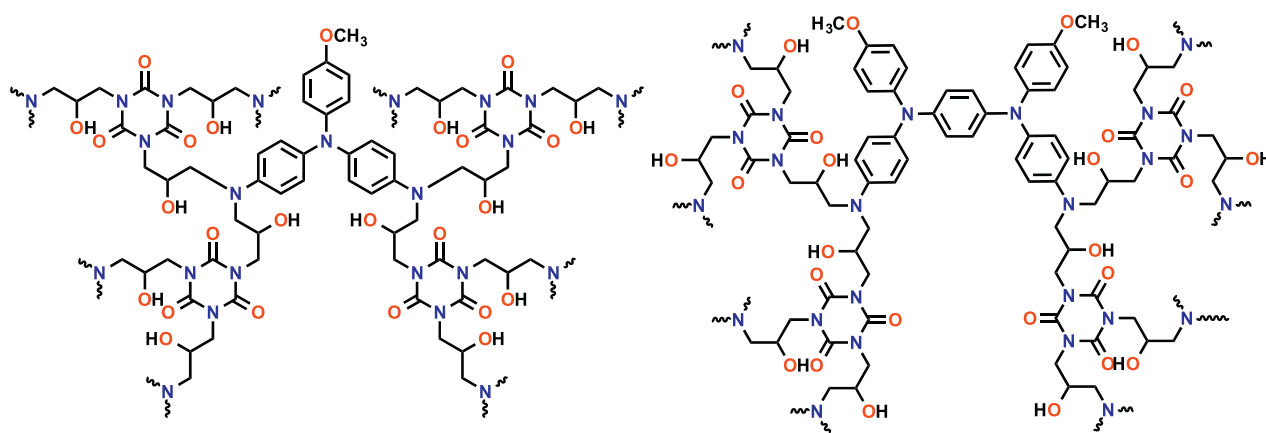
##### 2.4.3. Polyurethane

As high-performance materials, polyurethanes have gained increasing interest in a wide range of applications owing to their excellent elasticity, abrasion resistance, and broad substrate suitability. In the past 30 years, consideration about energy conservation has led them to a worldwide usage as thermal insulators, such as flexible substrates, plastic film, textile, coating and rubber.

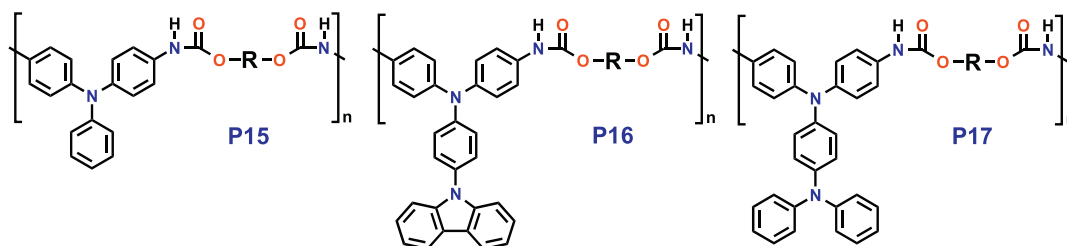
Niu and Wang reported three series of novel aromatic polyurethanes containing TPA derivatives via polycondensation of *N,N*-bis(4-isocyanatophenyl)aniline (**P15**), 4,4'-diisocyanato-4'-*N*-carbazolyITPA (**P16**), and *N,N*-bis(4-isocyanatophenyl)-*N,N'*-diphenyl-1,4-phenylenediamine (**P17**) with various dihydroxy monomers, respectively (Scheme 17) [172,173]. These highly stable anodic EC polymers, with excellent optical transmittance change, have been synthesized from addition-type isocyanates and different glycols. The resulting polymers exhibited high thermal stability, reversible electrochemical and EC characteristics under continuous cyclic redox scans.



**Scheme 15.** Representative scheme of TPA-based conjugate polymers.



**Scheme 16.** Representative scheme of TPA-based epoxy materials.

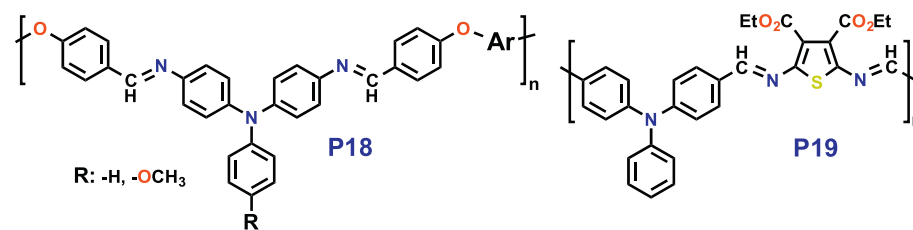


**Scheme 17.** Representative scheme of TPA-based polyurethanes.

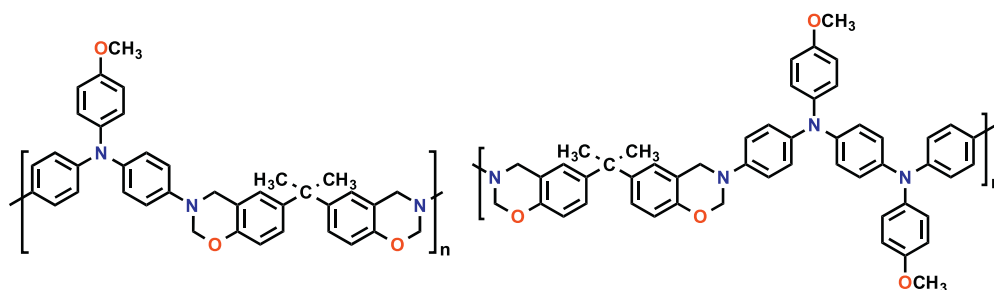
#### 2.4.4. Poly(azomethine)

Poly(azomethine)s or poly(Schiff-base)s with aromatic backbones are considered to be high performance polymers due to their high thermal stability, excellent mechanical strength, and

good optoelectronic properties. In recent years, poly(azomethine)s have also been explored for applications in organic electronics, such as light-emitting materials, pH sensors, and metal-collecting polymers. However, their insolubility in common organic solvents



**Scheme 18.** Representative scheme of TPA-based poly(azomethine)s.



**Scheme 19.** Representative scheme of TPA-based poly(benzoxazine)s.

limited their processability and application. Our group has successfully incorporated TPA units into poly(azomethine)s **P18** to increase the solubility, enhance the film-forming ability, and retain favorable thermal stability (Scheme 18) [174].

Skene et al. reported that polymerization of the robust polymer **P19** may be done directly on the working electrode by heating the comonomer coated substrate [175]. This on-substrate polymerization method boasts the advantage that either commercially available or easily prepared monomers may be used to synthesize stable electroactive polymers. The method is also potentially applicable to large scale and high throughput processing methods, such as roll-to-roll device fabrication, while being an environmentally friendly process, the main by-product produced during the polymerization is water.

Niu and Bai used the strategy to tune the band gap of poly(azomethine)s **P20** and **P21** by copolymerization of diamine with different conjugation dialdehydes [176]. The resultant poly(azomethine)s showed excellent thermal resistance and good solubility for polymer film formation via spin coating, and also exhibited stable and reversible EC properties with significant color change. The color of poly(azomethine)s could be varied from initial yellowish to red, violet or blue during oxidation.

#### 2.4.5. Poly(benzoxazine)

Poly(benzoxazine) is a well-established phenolic system with extensive interesting features and the capability to overcome limitations of traditional resole- and novolac-type phenolic-formaldehyde resins. These poly(benzoxazine)s possess several favorable advantages, including near-zero volumetric change upon curing, low water absorption, excellent heat resistance, catalysts-free for curing, free of toxic by-products during curing, good mechanical properties, high dimension stability, and low dielec-

tric constant. Therefore, poly(benzoxazine)s are popularly applied as encapsulation, electrical insulation, aeronautical and astronautical technologies.

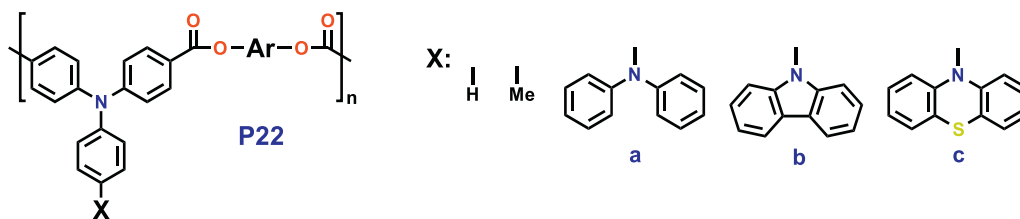
Two novel anodic TPA-containing EC poly(benzoxazine)s shown in Scheme 19 were successfully prepared in our group by the thermal curing reaction of the corresponding poly(benzoxazine) precursors, prepared by the reacting paraformaldehyde with TPA-based diamines and bisphenol A [177]. The thermally stable TPA-based poly(benzoxazine)s revealed interesting multi-EC with highly optical contrast in both visible and NIR ranges. The TPA-based EC poly(benzoxazine) precursors and poly(benzoxazine)s were investigated for the first time. The TPA-based poly(benzoxazine) precursors reveal lower oxidative potentials and increased coloring stages compared with their corresponding PAs.

#### 2.4.6. Polyester

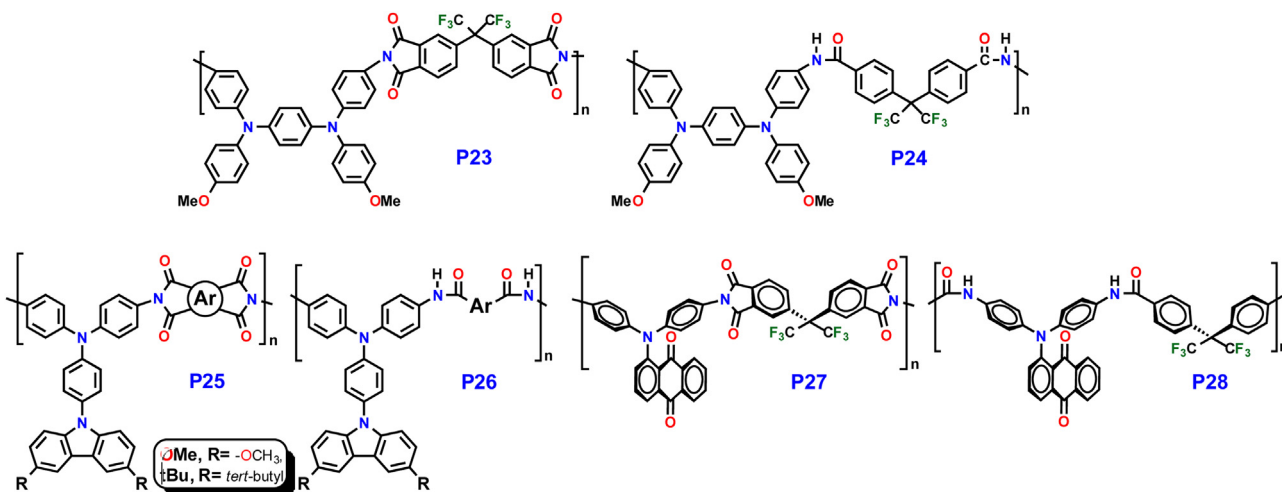
It is well known that wholly aromatic polyesters (polyarylates) possess high thermal stability, optical transparency in visible light region, and excellent mechanical properties. However, the high melting temperatures or softening temperatures and limited solubility in organic solvents of most polyarylates make their processing difficult unless flexible spacers are included in the systems, thereby lowering the thermal stability. Interest in molecular engineering of physical properties for high-performance polyarylate persists because small alternation of molecular structure of a polymer can dramatically influence performance and processing properties.

Therefore, TPA-based polyarylates **P22** [178] (and pendant diphenylamine **P22a** [179], carbazole **P22b** [180], or phenothiazine **P22c** [181]) were synthesized from the respective dicarboxylic acids and various bisphenols monomers (Scheme 20). The excel-





Scheme 20. Representative scheme of TPA-based polyarylates.



Scheme 21. Representative TPA-based polyimides with electric switching mechanism of conformational change.

lent solubility in common organic solvents makes the polyesters facilitates the formation of films and devices. They also exhibit electrochemical stability with a reversible redox and multi-EC behaviors, even after many times cyclic switches, thus candidates as anodic EC materials.

### 3. Triphenylamine-based resistive switching polymeric memory devices

Devices fabricated from switchable resistive materials are generically categorized as resistive random access memory (RRAM), or resistor-type memory. Unlike capacitor and transistor memories, it is not necessary for a resistor-type memory to have a specific cell structure (e.g., a field-effect transistor) or to be integrated with the complementary metal-oxide-semiconductor technology.

RRAMs usually store data by recording the electrical bistability at high and low conductivity (ON and OFF) states as “1” and “0”, respectively, arising from intrinsic property changes of materials, such as redox (reduction-oxidation), CT, phase and conformation changes, responding to an electric field or applied voltage. Therefore, the design and synthesis of materials for RRAMs are very important. As memory materials, polymers, organic molecules, inorganic materials, and inorganic/organic hybrid materials have been successfully developed and used in resistive memory devices.

Thanks to the favorable properties of flexibility, ease of processing, 3D-stacking capability, good scalability, large capacity for data storage, and low cost, polymeric resistive memory would be expected to be a promising alternative to the conventional inorganic semiconductor-based memory technology. Extensive studies toward new polymer materials and device structures have been carried out to enhance memory performance, such as large ON-OFF current ratio, low operation voltage, relatively long retention time, and high operation endurance [182,183].

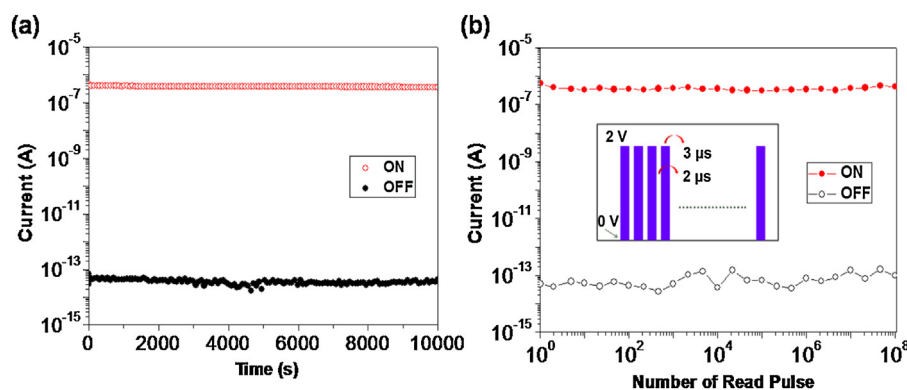
#### 3.1. Mechanism

Considerable research has been dedicated to investigate the electric switching behavior of polymer memory devices. Although still controversial, research has already led to several hypotheses of electric switching mechanisms based on advanced analytical techniques, experimental results, and theoretical simulations [183–191]. The most widely used mechanisms in HPP resistive memory devices are described, such as CT, space charge traps, and filamentary conduction.

Volatile memory devices retain the steady state condition for a period of time after the power is turned off, subsequently returning to the OFF state. Nevertheless, continuously applying the potential pulse will maintain the ON state. The volatile memory effects, dynamic random access memory (DRAM) and static random access memory (SRAM), can be divided by the retention time of the ON state after removing the applied voltage. A non-volatile memory device can stay in the ON state steadily without an applied voltage bias, with behavior that may be divided into two classes, namely write-once read-many times (WORM) memory and rewritable (Flash) memory, depending on whether a suitable voltage can switch the ON state to OFF state.

##### 3.1.1. Charge transfer

CT can be characterized as a process of partial transfer of electronic charge from the donor (D) to the acceptor (A) moieties in the electron D-A system by applying a suitable voltage, resulting in a sharp increase in conductivity [192]. In order to obtain a better understanding of switching mechanisms, several study methods, such as density functional theory calculations, UV/Vis absorption spectra, in situ fluorescence spectra, and transmission electron microscope techniques, may be used to investigate and explain the CT phenomenon [193–196]. CT is anticipated to occur most frequently in the polymers with D-A structures [197–199].



**Fig. 6.** (a) Effect of operation time on the ON and OFF states of the ITO/P23 (50 nm)/Al device with a continuous  $-2$  V. (b) Stimulus effect of read pulses on the ON and OFF states of the P23 (50 nm) device. The insert shows the pulse shapes of the measurement. [201], Copyright 2011. Reproduced with permission from John Wiley & Sons Inc.

The memory behaviors based on the D-A polymers, may be tuned through the modifications on polymer structures. By tuning the electron-donating or -accepting capability of D-A polymers, different memory behaviors can be achieved [200]. The strong dipole moment in polymer is also beneficial to maintain the conductive CT state, usually leading to a non-volatile behavior. Otherwise, the conductive CT state is not stable after removal of the electric field and a volatile memory behavior will be observed, as the dipole moment is so weak.

**3.1.1.1. Conformational change.** A conformational change is an extensively applied mechanisms in polymer memory devices. The onset of such effects between TPA donor and hexafluoroisopropyl bis(phthalic dianhydride) (6FDA) acceptor were examined for memory applications using the functional PI P23 and the PA P24 comprising electron-donating TPPA. These exhibited DRAM and SRAM behaviors, respectively (Scheme 21) [201]. The phthalimide units in P23 form a plane with dihedral angles of  $179.5^\circ$  to adjacent phenyl ring that occur the back CT; nevertheless, the conformation of *N*-phenylbenzamide in P24 is a non-planar structure that will block the back CT and result in longer time at the conductive state for PA as SRAM after removing external voltage.

The memory device was initially switched to a high or low conductivity state, respectively, and then applying a constant stress of  $-2$  V. No obvious degradation in current was observed at ON and OFF states for at least 104 s during the readout test. Furthermore, the ON and OFF state were stable up to  $10^8$  read pulses of  $-2$  V as shown in Fig. 6. (The pulse period and width are 3 and 2  $\mu$ s, respectively, as shown in the inset)

A similar concept was used to prepare 4-(*N*-carbazolyl)TPA-based (P25 and P26) [202] and 1-anthraquinone-substituted HPPs (P27 and P28) [203]. All the results further confirmed that the non-planar linkage and high dipole moment of PAs could effectively extend the retention time than that of the analogous PIs.

**3.1.1.2. LUMO energy level.** The lowest unoccupied molecular orbital (LUMO) energy is also an important parameter for producing a conductive state. The lower LUMO energy level provides a more stable CT state since the CT state is a meta-stable state. Our group therefore synthesized and demonstrated systematic studies of functional PIs P29 [198] containing various dianhydrides such as 6FDA, oxydiphthalic dianhydride (ODPA), 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA), pyromellitic dianhydride (PMDA), and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NPDA) (Scheme 22). The electron-withdrawing feature of PIs increased with lowered LUMO energy level and the retention time of their memory devices were further increased. Thus, the

memory characteristics could be tuned from DRAM to SRAM or WORM.

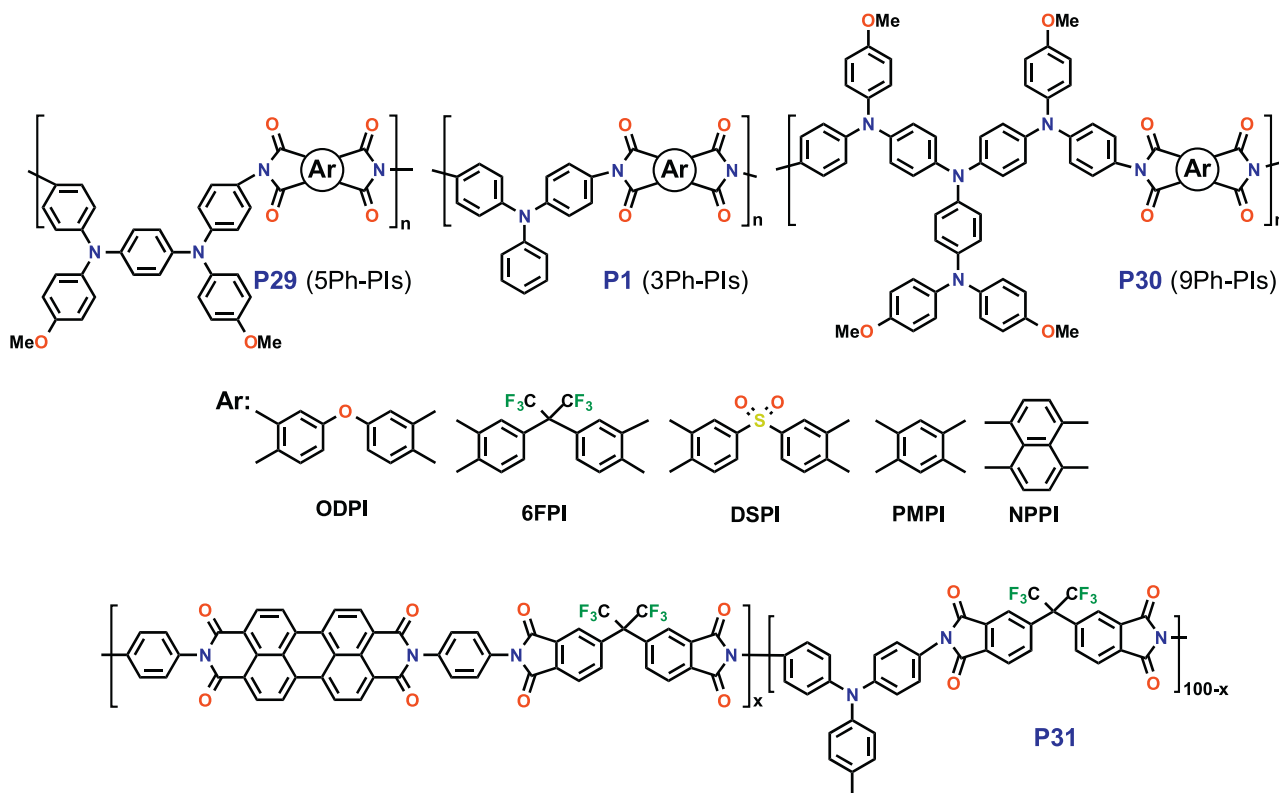
**3.1.1.3. HOMO energy level.** The Liou group reported the synthesis of 3Ph-PIs (P1), 5Ph-PIs (P29), and 9Ph-PIs (P30) with gradually increased electron-donating ability and their corresponding memory devices [204]. With the electron donating ability increasing from P1 through P29 to P30, the memory devices exhibited an increased retention time. For example, the PIs with the 6FDA revealed DRAM behavior for P1-6FPI and P29-6FPI, while P30-6FPI exhibited SRAM response. Therefore, the memory behaviors can be fine-tuned by judiciously designing the chemical structure to achieve different retention times.

**3.1.1.4. Dipole moment.** The Liou group reported an exception in behavior from mechanisms involving energy-level effects [198]. Although P29-DSPI has a higher LUMO energy level than P29-PMPI, it exhibits non-volatile rather than that would be anticipated volatile behavior based solely on relative energy levels. This conflict between memory characteristic and LUMO energy is ascribed to a dipole moment effect. The major difference between P29-DSPI (5.45 Debye) and P29-PMPI (3.70 Debye) is the higher dipole moment of the former. Therefore, the more stable CT states were formed by a higher dipole moment, resulting in non-volatile memory behavior.

**3.1.1.5. Large conjugation.** The introduction of a highly electron affinitive or large conjugated unit is an effective and simple method to develop non-volatile memories (Scheme 22) [205]. For example, the introduction of a small amount of the perylene bisimide (PBI, i.e., 5 mol%) significantly altered the memory behavior from volatile DRAM to non-volatile WORM (the case of P31), attributed to the separated charge trapped by the deep LUMO energy level and also stabilized by the large conjugation resulting from the electron affinitive PBI.

### 3.1.2. Space charge traps

The carriers near the electrode can accumulate and build up a space charge if the interface between electrode and polymer is ohmic and the polymer is trap-free. Mutual repulsion between individual charges restricts the total charge injected into the polymer, and the resulting current is defined as space charge-limited current (SCLC). Space charges in materials may occur from several sources, such as (1) electrode injection of electrons and/or holes, (2) ionized dopants in interfacial depletion regions, and (3) accumulation of mobile ions at electrode interfaces. Traps may be present in the bulk materials or at interfaces, and result in lower carrier mobility. When present at interfaces, they may also affect



**Scheme 22.** Representative TPA-based polyimides with electric switching mechanism of donor effect and conjugation.

charge injection into the materials. The electrical switching behavior of some polymeric materials has been associated with SCLC [194].

### 3.1.3. Filament conduction

When the ON state current is highly localized to a small area within the memory device, the resulting phenomenon can be called “filament conduction”. It has been suggested that filament conduction is confined to device physical damages in RRAMs. Two types of filament conduction have been widely reported in polymer resistive memory devices; the formed filaments could be observed under an optical microscope or scanning electron microscope [206,207]. One type is the carbon-rich filaments formed by the local degradation of polymer films [207,208]. The other is associated with the metallic filaments that result from the migration of electrodes through the polymer films [209,210]. For the filamentary conduction, the polymers with both the coordinating atom and  $\pi$ -conjugation can bind to metal ions, regardless of the binding sites (side chain or main chain), are essential for the production of metal filaments [183,211]. Therefore, the filamentary conduction mechanism has been often suggested to explain switching phenomena observed in a variety of polymer memory devices.

## 3.2. HPPs for volatile memory devices

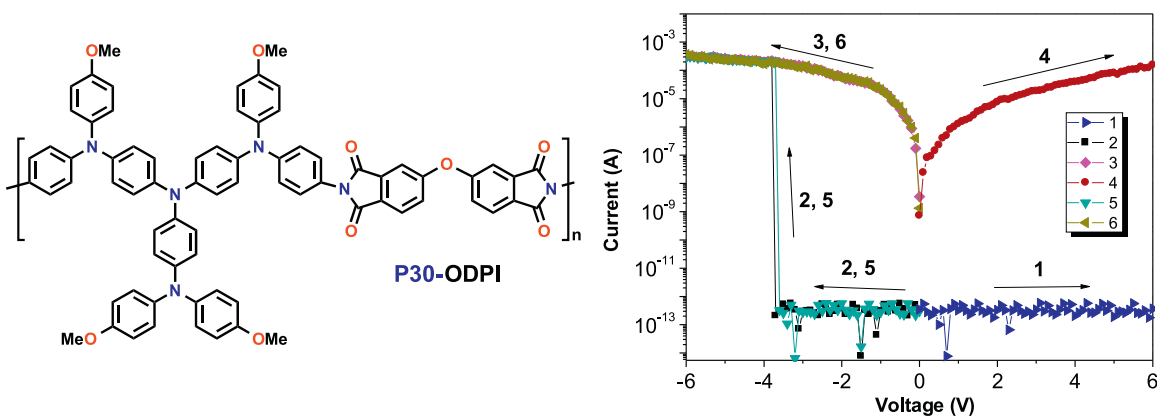
A volatile memory device that remains in the ON state for a short period after the removal of applied voltage (less than 1 min) is denoted by the acronym DRAM (Fig. 7) [204]. On the other hand, the device with a longer retention time than a DRAM device in the ON state after turning off the power is denoted by the acronym SRAM (Fig. 8) [204]. Nevertheless, the SRAM memory device is still volatile and will return to the OFF state without an erasing process, despite the longer retention time at the conductive state.

### 3.2.1. DRAM properties

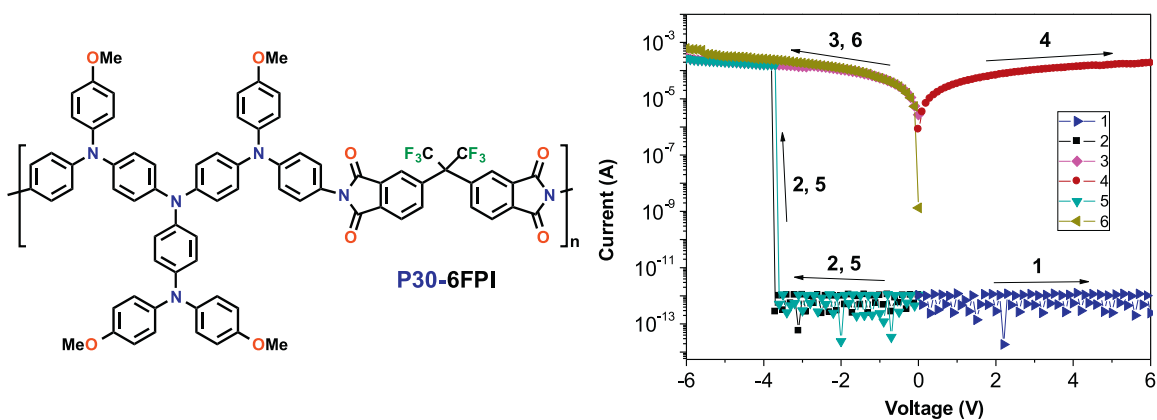
The Kang group [193] first pointed out the DRAM memory characteristic for a TPA-based PI **P32** based on the CT mechanism (Scheme 23) with the device configuration of Al/**P32**/ITO. From the experimental results, the memory device remained at ON state during the subsequent positive scan with a high ON/OFF current ratio up to  $10^5$  after switched from an OFF state to ON state. The memory device based on PI **P32** revealed an erasable memory property by switching back from ON state to OFF state during the subsequent negative sweep. The memory device with volatile DRAM behavior (relaxed from ON to OFF state in 1 min) can be further reprogrammed to its ON state. Furthermore, by refreshing a potential pulse of 1 V every 5 s, the ON state can be electrically maintained. The resulting DRAM behavior was due to the formation of unstable CT state and could be referred to the theoretical calculations. Compared with **P32**, PI **P33** with TPA-substituted diphenylpyridine moieties reported by Kang et al. [212] also reveals DRAM property with a more volatile (less stable) ON state and the lower threshold voltage.

### 3.2.2. SRAM properties

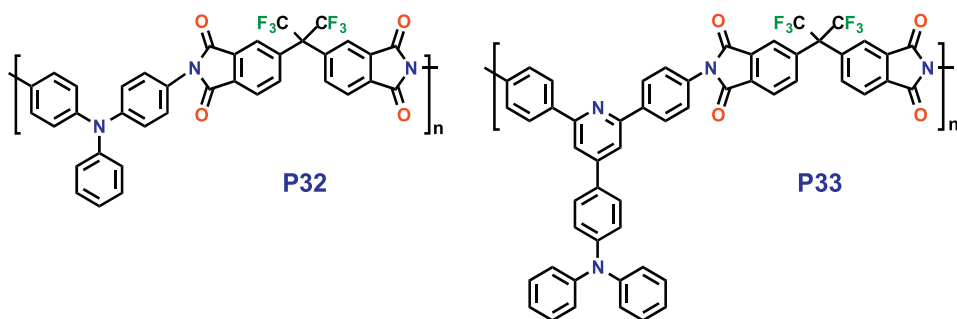
A functional TPA-based PI **P34** bearing pendent electron-donating carbazole moiety and electron-accepting 6FDA was first reported by our group (Scheme 24) [63]. The memory device fabricated by the Qi group [213] as a simple ITO/**P34**/Au sandwich structure exhibits bi-directionally attainable ON states by switching both positive and negative scans with the achievement of an ON/OFF current ratio as high as about  $10^5$ . Furthermore, by periodically applying read pulse of -1 V, both the ON and OFF states were stable and can survive up to  $10^8$  read cycles. The memory device agrees well with the SCLC model at the OFF state and turns to the Ohmic conduction model on the ON state. The molecular simulation is applied to elucidate memory mechanism of the D and A units in the electroactive PI.



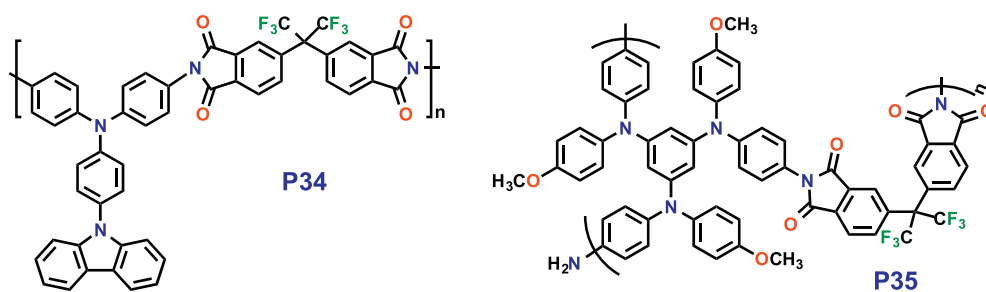
**Fig. 7.** Current-voltage (*I-V*) characteristics of ITO/P30-ODPI (~50 nm)/Al memory device. [204], Copyright 2013. Reproduced with permission from the Royal Society of Chemistry.



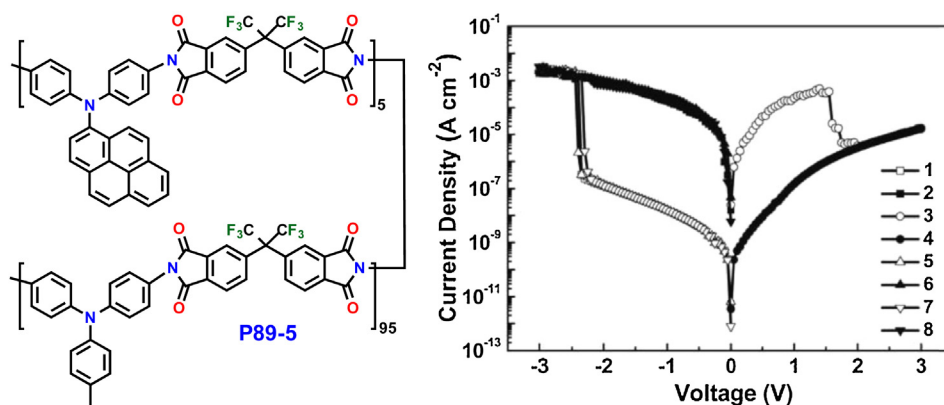
**Fig. 8.** Current-voltage (*I-V*) characteristics of ITO/P30-6FPI (~50 nm)/Al memory device (The fifth sweep was conducted after turning off the power for 3 min). [204], Copyright 2013. Reproduced with permission from the Royal Society of Chemistry.



**Scheme 23.** Chemical structures of typical polyimides reported for volatile memory devices with DRAM properties.



**Scheme 24.** Chemical structures of typical polyimides reported for volatile memory devices with SRAM properties.



**Fig. 9.** Current-voltage ( $I$ - $V$ ) characteristics of the ITO/**P89-5** (~50 nm)/Al memory device. [215], Copyright 2012. Reproduced with permission from the Royal Society of Chemistry.

Guan et al. reported a hyperbranched PI (**P35**) [214] by reacting the triamine monomer with 6FDA. The memory device exhibited SRAM behavior with a relatively low switching voltage of  $-1.90$  V. Moreover, the device showed good stability in both the OFF and ON states, which could be retained as long as  $10^4$  s under a continuous voltage stress of  $-1.00$  V with an ON/OFF current ratio reaching up to  $10^6$ . Molecular simulation results suggested that efficient CT between the triamine moieties and 6FDA moieties, which is responsible for the improved electrical memory performance.

### 3.3. HPPs for non-volatile memory devices

In a non-volatile memory device, if the ON state can be switched to OFF state by applying a reverse voltage in an erasing process, the memory behavior is called a rewritable memory (Fig. 9) [215]. On the contrary, a WORM memory is able to maintain the ON state of permanently and may be read repeatedly even applying a reverse potential (Fig. 10) [204].

#### 3.3.1. WORM properties

The Ree group reported a TPA-based PI **P36** (Scheme 25) bearing a hydroxyl group [216], and its memory device with the configuration of ITO/**P36**/Al. The device exhibited a WORM memory property with a low threshold voltage, long retention time, and high ON/OFF ratio. Especially, the thermally stable PI-based memory device persists its WORM property even at operation temperature up to  $150$  °C. According to the fitted  $I$ - $V$  data, the trap-limited SCLC mechanism is dominant when a device is in the OFF state. In addition, the filament formation within the active layer was found to cause the ON-state current level of memory device to be independent of the size of device cell. The filaments lead to the ON state by acting as channels through the carriers flow via hopping process.

Wang et al. [217] synthesized a functional PI **P37**, which shows excellent thermal stability and high glass transition temperature  $T_g$ . The **P37**-based memory devices revealed symmetric bistable WORM memory behavior, and the ON state of the device withstood a constantly applied potential of  $-1$  V and  $10^8$  pulse read cycles under ambient conditions. The electric field-induced ET from the TPA donor to the phthalimide acceptor through the oxadiazole spacer resulting in the WORM memory property. Two series of TPA-based PIs **P38** and **P39** with triazole substituents were further prepared [218,219], and the **P38**-based memory device showed nonvolatile WORM memory property accompanied with good stability and high ON/OFF current ratio. Conformation-coupled CT, which further proved by theoretical calculations, can probably be observed under an electric field between electron donor TPA and the electron acceptor phthalimide with a single or ether bond link-

age. A large potential energy barrier resulting from the twisted molecular chain in the CT state usually dissociate the CT complexes and stabilize the CT state, thus retaining the ON state. The carriers will move to both directions once a high-conductive state is formed and the reverse bias could not turn the device back to the OFF state.

Qi et al. reported a TPA-based aromatic hyperbranched PI **P40** with electron-accepting 6FDA species [220], and a memory device (ITO/**P40**/Au sandwiched) exhibiting two obvious, but irreversible conductive states with an ON/OFF ratio of 300.

The irreversible and nonvolatile WORM memory property was attributed to the electric-field-induced CT between TPA and 6FDA groups, and the charge-separation state of the generated CT complexes retained by strong electron-withdrawing 6FDA moieties.

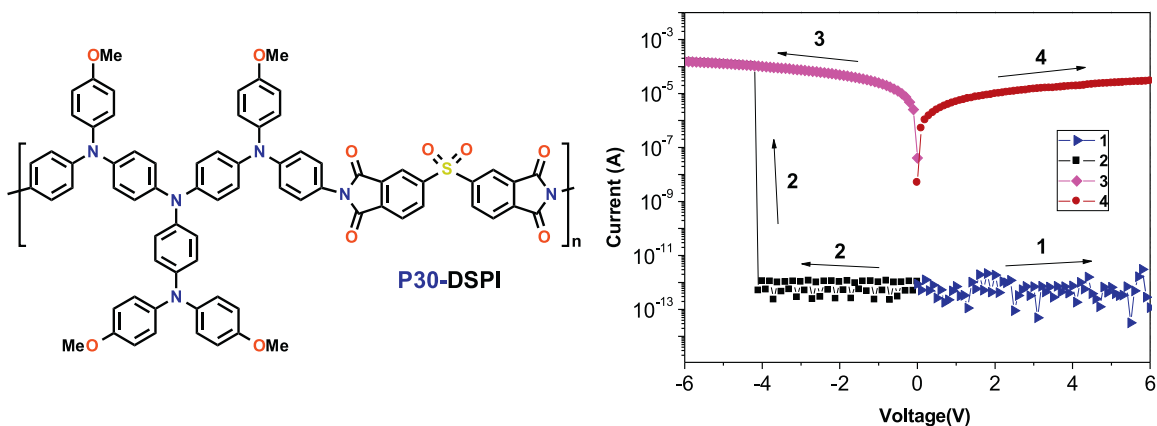
Our group recently reported TPA-based PIs with the incorporation of cathodic EC viologen group for both multicolored EC and polymeric memory applications [73]. The isolated flexible ethyl-linkage might block the back CT between TPA and heptyl viologen (HV) units, resulting in an extended retention time of the prepared memory device after removing the applied potential. Therefore, the thermally stable PI **P41** with strong D-A CT possesses WORM memory behavior with excellent operation stability.

Niu and coworkers reported three series of TPA-based polyurethanes **P42-P44** synthesized from the corresponding addition-type isocyanates and different glycols [172,221]. The polymers exhibited excellent thermal stability, reversible electrochemical behavior, continuous cyclic stability of EC characteristics, and non-volatile WORM memory behaviors resulting from the isolated D-A characteristics.

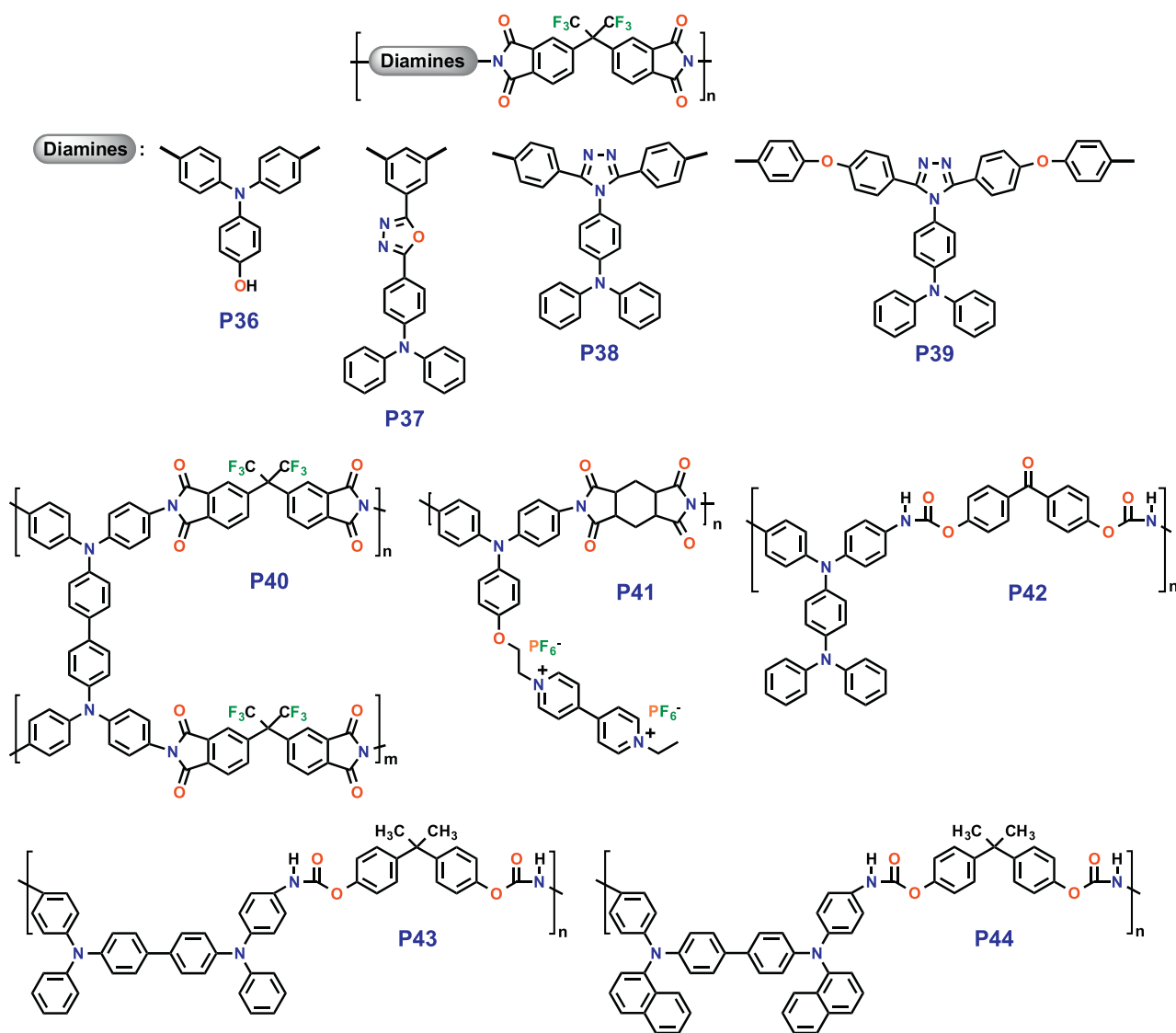
#### 3.3.2. Flash properties

Four PIs containing carbazole (**P45**) [222], diphenylcarbamyloxy (**P46**) [223], diphenylaminobenzylidenylimine (**P47**) [224], and anthracene (**P48**) [225] at the side chains with changes in hole-transporting and electron-donating moieties are reported for application as rewritable memory devices (Scheme 26). For example, **P45**-based memory device reveals unipolar ON and OFF switching property with a high ON/OFF current ratio and very low power consumption [222]. A memory device based on **P46** exhibited a long retention time, low threshold voltage, and high ON/OFF current ratio [223]. In addition, the local filament formation and Schottky emission within **P47**-based memory device resulted in a rewritable memory [224]. A **P47**-based memory device (Al/**P48**/Al sandwiched) exhibited rewritable and nonvolatile memory properties with a very small voltage range and a high ON/OFF ratio. Within polymer **P48**, the hole trapping anthracene moieties and the electron trapping phthalimide groups play significant roles for its memory behaviors.





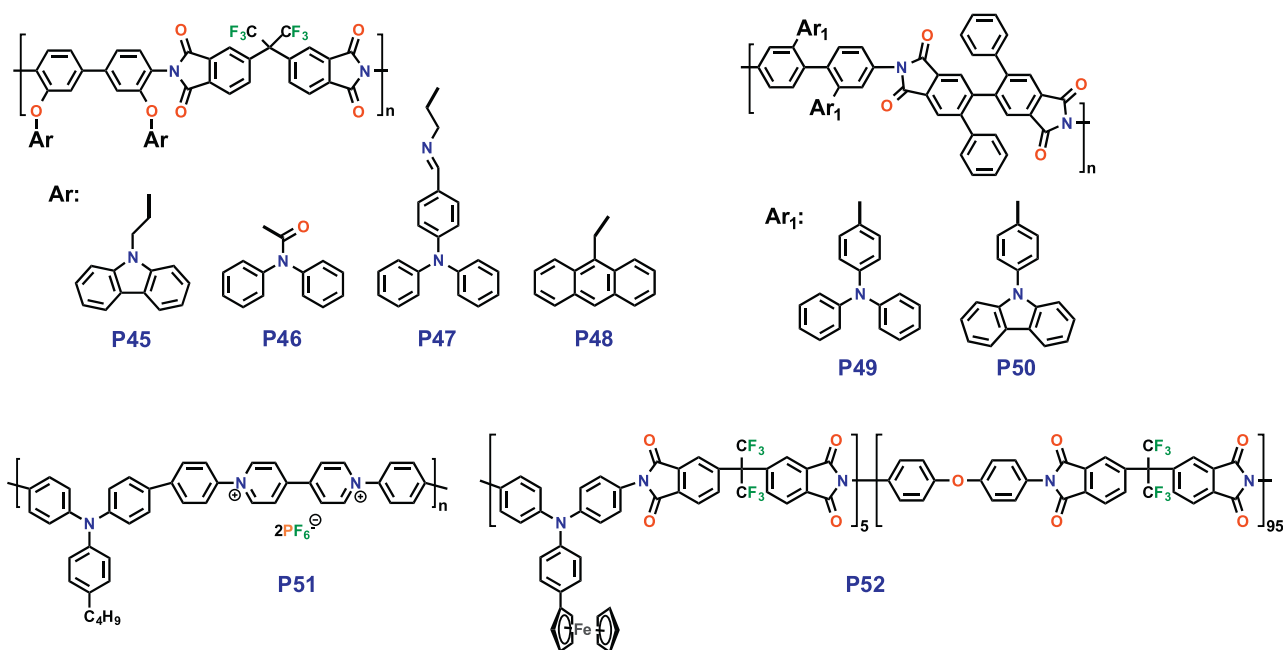
**Fig. 10.** Current-voltage ( $I$ - $V$ ) characteristics of the ITO/P30-DSPI (~50 nm)/Al memory device. [204], Copyright 2013. Reproduced with permission from the Royal Society of Chemistry.



**Scheme 25.** Chemical structures of typical polyimides reported for nonvolatile memory devices with WORM properties.

On the other hand, the Shen group [226] fabricated two memory devices, based on PIs **P49** and **P50** with donors TPA or carbazole as pendant groups, respectively. The PIs **P49** and **P50** with excellent

thermal stability and showed good solubility and their memory devices (Al/Pis/ITO sandwiched) revealed unipolar rewritable flash and bipolar rewritable flash memory characteristics, respectively.



**Scheme 26.** Chemical structures of typical polyimides reported for nonvolatile memory devices with Flash properties.

Memory devices based on **P49** and **P50** both fit the ohmic model at the ON-state, but fit different models in the OFF state, with **P49** and **P50**, respectively, to the Schottky emission and SCLC models in the OFF state, with ON/OFF current ratios of about  $10^4$ .

A novel soluble viologen-based conjugated ionic polymer **P51** [227] was synthesized by using Suzuki coupling reaction in the presence of the tetrakis(triphenylphosphine)palladium(0) as the catalyst. A typical nonvolatile rewritable memory behavior was observed with low turn-on and turn-off voltages and a large ON/OFF current ratio of more than  $10^5$ .

A functional PI **P52** [228] has been reported with TPA pendent ferrocene (Fc) group as the electron donor entity, oxydianiline as the flexible unit and 6FDA as the electron acceptor. **P52** exhibited flash memory behavior with excellent long-term operation stability and ultrafast response speed. The simulation results reveal that the Fc species contribute significantly to the donating electrons. The electron-excitation-accompanied conformation twist is suggested to provide an energy barrier and stabilize the formed CT complex, endowing the **P52** with nonvolatile memory.

### 3.4. Molecular design on volatility

As described in the preceding, the writing operation of resistive memory device switches between the OFF and ON states is performed by applying a pulse or voltage bias to the device. Further, memory devices can be distinguished to be volatile or non-volatile based on whether the external voltage is necessary retaining the ON state or not. As presented in the following memory properties can be fine-tuned by several approaches, such as changing the linkage, conformation, film thickness, and electron donor or acceptor within the active polymer layer [198,229–233].

#### 3.4.1. Donor effect

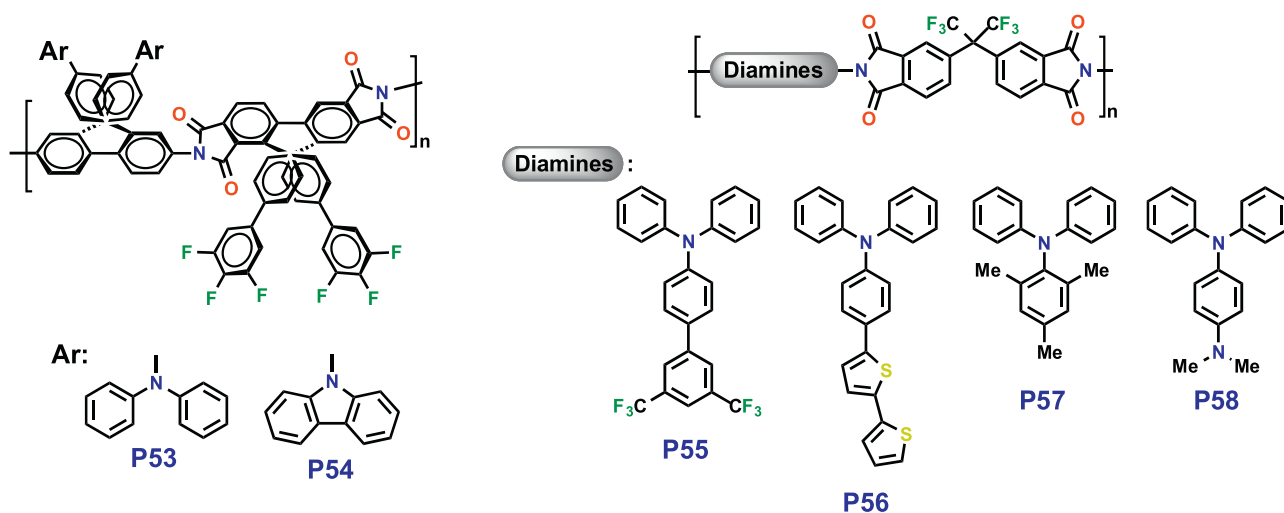
Shen et al. [195] synthesized thermally stable polymers **P53/P54** containing electron donor TPA/carbazole and electron acceptor phthalimide groups (Scheme 27). Memory devices based on **P53** and **P54** with Al/polymer/ITO sandwiched structure showed flash memory and excellent WORM memory performance, respectively. High ON/OFF current ratios and long retention times could be

realized, even when operating in the ambient conditions without encapsulation.

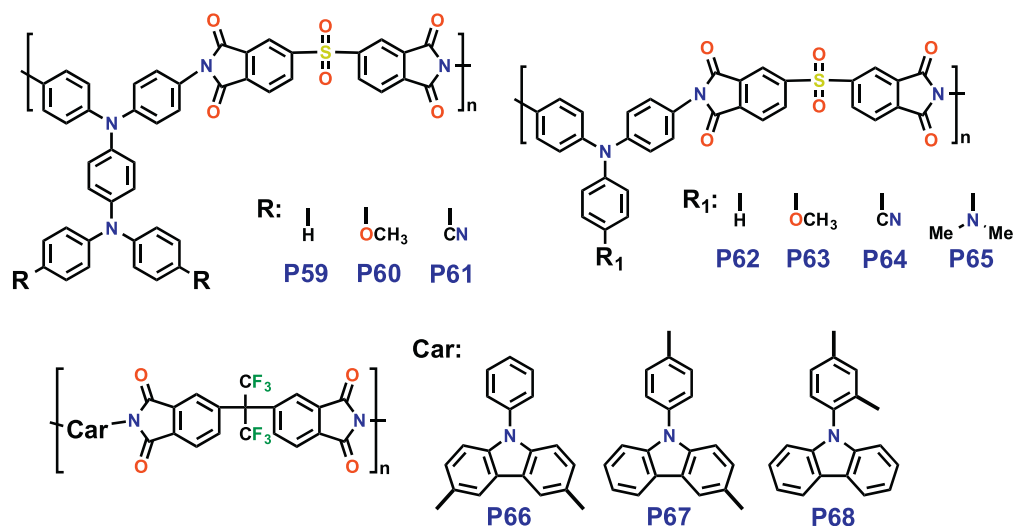
Aromatic TPA-based PIs with either the electron acceptor bis(trifluoromethyl)phenyl group (**P55**) or the electron donor bithiophene group (**P56**) were prepared; both exhibited high thermal and dimensional stability [234]. Under positive and negative voltage sweeps, the Al/PI/Al devices demonstrated various memory behaviors (volatile DRAM and nonvolatile WORM memory). The stability of the CT state of memory device was increased by introducing the electron-donating bithiophene moieties with high nucleophilicity and aromaticity. On the contrary, the memory behavior was altered in a negative way by incorporating the bis(trifluoromethyl)phenyl substituents to reduce the nucleophilic capability. All of the PI films revealed high ON/OFF current ratios ( $10^5$ – $10^8$ ) and high stability in the ON or OFF state even without encapsulation.

Lee et al. reported two TPA-based PIs (**P57** and **P58**) containing different donating groups to fine-tune the polymer structures and their corresponding memory properties [231]. The memory devices based on **P57** and **P58** with Al/PI/Al configuration exhibited an unipolar WORM and bipolar switching memory properties, respectively, as well as excellent stability in the ON/OFF state and high ON/OFF current ratio up to  $10^8$ – $10^9$  even under ambient condition. The memory properties of **P57**- and **P58**-based memory devices originate, respectively, from TPA with three methyl groups and dimethylamine moieties, which act as charge-trapping sites and enhance the electron-donating ability of PIs (Scheme 27). The result shows that changing the functionality on the TPA unit can alter the memory properties.

Three functional PIs, **P59**–**P61**, bearing conjugated bis(triphenylamine) derivatives with electron-donating and accepting substituents were synthesized (Scheme 28) [235]. All the PI-based memory devices with Al/PI/Al sandwiched structures exhibited high resistances in the OFF-state. The memory devices based on PI **P60** (with electron-donating methoxy groups) and PI **P61** (containing electron-accepting cyano substituents) showed nonvolatile WORM and volatile DRAM properties, respectively. The memory behaviors were governed by a mechanism involving local filament formation and trap-limited SCLC, taking the work



**Scheme 27.** Molecular design on the volatility of TPA-based polyimides through donor effect.



**Scheme 28.** Molecular design on the volatility of TPA-based polyimides through donor effect.

function of the metal electrodes, possible trapping sites, chemical nature, substituent effect, and molecular orbital levels of the PIs into consideration.

A series of thermally and dimensionally stable DSDA-based PIs **P62–P65** [236] bearing three different TPA derivatives were synthesized for further study of donor effects on the memory performances. The memory devices based on PIs **P62–P65** with device configuration of Al/Pis/Al revealed various memory properties according to the functionalities of the TPA groups. Notably, for PI **P64** with cyano groups serving as electron-accepting units and charging sites, around 80% of the device cells exhibited WORM memory property and the rest revealed DRAM memory performance.

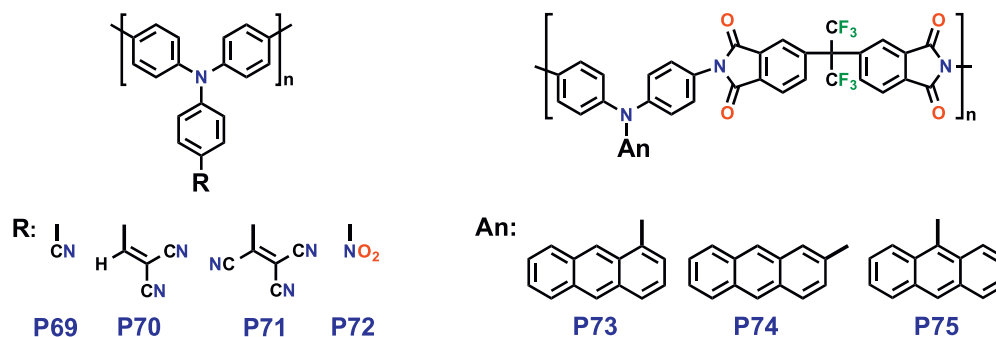
Three isomeric PIs synthesized, **P66–P68**, demonstrated, respectively, volatile SRAM (retention time: 1 min), SRAM (retention time: 5 min), and nonvolatile WORM behavior [237]. Isomerization could significantly alter the conjugated molecular backbone of the electroactive PIs. **P66** possesses the best structural coplanarity, which greatly facilitates its CT and back CT process, leading to the volatile SRAM feature. The backbone structure of the **P67** becomes rather twisted, which consequently hinders the charge transition along the main chain, resulting in a SRAM effect with extended retention time. In contrast, the **P68** exhibits vastly different backbone struc-

ture, where the primary electron-donating unit (carbazole unit) is excluded from the conjugated main chain and presents as a pendant. The large dihedral angle between the pendant electron donor and the backbone hinders the CT process and prohibits the back CT process, accounting for its non-volatile WORM behavior. Besides, optical measurements indicate the formation of more stable CT complexes in the **P68** than those in the **P66** and **P67**, consistent with their non-volatile and volatile memory characteristics.

Another aromatic and thermally stable PI **P30** with highly electron-donating starburst triarylamine group was designed and synthesized by the Liou group [204]. The radical cation in the resulting PI could be stabilized by incorporating the starburst triarylamine group as well as the enhanced solubility and film-forming capability. In addition, the corresponding **P1** (3Ph-PIs) and **P29** (5Ph-PIs) were synthesized to study the donor effects on their memory behavior. The results demonstrated that the retention time of the memory devices exhibit a systematic enhancement by increasing the electron donating ability from **P1** to **P29** and then to **P30**.

#### 3.4.2. Acceptor effect

A series of polyTPAs (**P69–P72**) [238] with pendent acceptors (cyano, dicyanovinyl, tricyanovinyl, and nitro) have been



Scheme 29. Molecular design on the volatility through acceptor effect.

synthesized by oxidative coupling polymerization using  $\text{FeCl}_3$  as oxidant. The tunable memory properties of the ITO/polymer/Al sandwiched memory devices, including DRAM, SRAM, and WORM, were achieved by introducing acceptors with different extent of electronic delocalization and electron-withdrawing intensity into the polyTPAs. The highly fluorescent **P69** exhibited volatile DRAM memory characteristic because of the large band gap and weak intramolecular CT capability. **P70** and **P71** showed volatile SRAM memory properties with retention time of 5 and 14 min, respectively, depending on electron-withdrawing capability of the acceptors. **P72** afforded nonvolatile WORM memory behavior attributed to the trapped charge in the nonconjugated nitro group even though the dipole moment and electron-withdrawing capability of nitro group were weaker than that of cyanovinyl groups. Moreover, except for the devices derived from cyano-containing ambipolar polymers **P69–P71** could be switched to the ON state and exhibited WORM memory behavior in positive unipolar  $I$ - $V$  switching. This phenomenon indicated that the Al atoms preferentially interact with polyTPAs containing cyano than nitro substituents.

Three functional PIs **P73–P75** in which the diphenylaminoanthracene group served as the electron donor and 6FDA served as the electron acceptor were synthesized [239]. The only difference between the three PIs was that the anthracene group was attached to the nitrogen atom through different tethering positions (1-, 2-, and 9-). Characterization showed that the **P73** and **P75** based memory devices exhibit nonvolatile WORM behavior, while the **P74**-based memory device exhibits volatile SRAM behavior. Quantum chemical calculation results indicate that a smaller dihedral angle between the anthracene and diphenylamine units of **P74** caused better coplanar structure for CT and back CT processes, which accounts for the observed volatile SRAM memory performance. All of the PIs possess excellent long-term operational stability (Scheme 29).

A series of hyperbranched PIs **P76** was synthesized by reacting a triamine monomer with various dianhydrides [240]. All the hyperbranched PIs exhibited excellent organosolubility and high thermal stability. Memory devices with a sandwiched ITO/**P76**/Al structure were constructed using **P76** as the active layers. All the **P76**-based memory devices exhibited favorable memory performances, with switching voltages between  $-1.3$  V and  $-2.5$  V, ON/OFF current ratios up to  $10^7$  and retention times long to  $10^4$  s. Tunable memory characteristics from electrical insulator to volatile memory, and then to nonvolatile memory were obtained by adjusting the electron acceptors of **P76**. Molecular simulation suggested that the electron affinity and the dipole moment of the **P76** were responsible for tuning the memory characteristics. With the electron affinity and dipole moment of the **P76** increasing, the memory characteristics turned from volatile to nonvolatile.

Moreover, three aromatics hyperbranched PIs **P77** using phthalic anhydride (PTA), 1,8-naphthalic anhydride (NA) and 3,4-perylenedicarboxylic anhydride (PEA) as endcapping reagents are

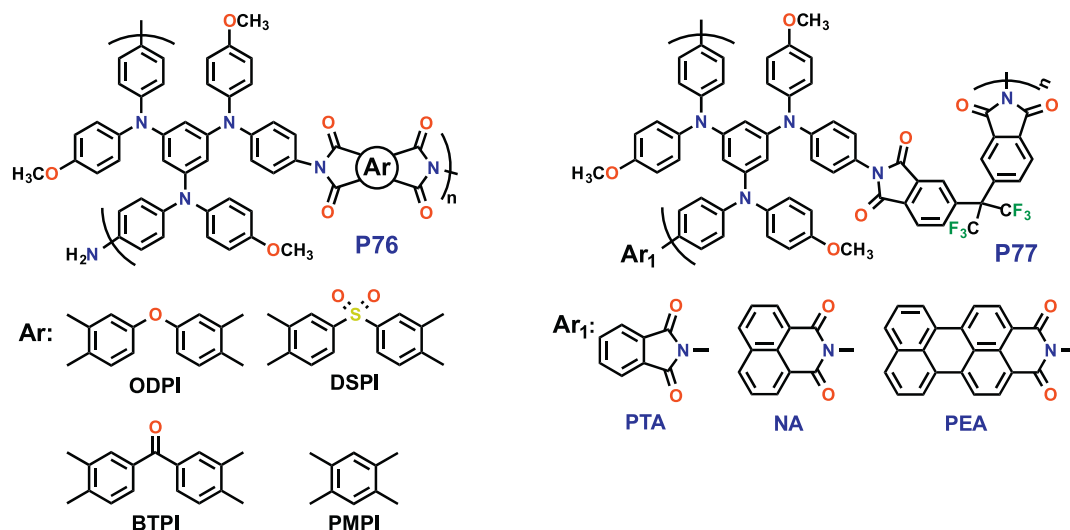
explored as polymer memory materials [241]. All these hyperbranched PIs showed excellent solubility in various organic solutions. Tunable memory characteristics from volatile to nonvolatile were obtained by adjusting the endcapping groups. Compared to **P77-PTA**, **P77-NA** and **P77-PEA** exhibited enhanced nonvolatile memory behaviors with switch voltages as low as 0.8 V, and outstanding thermal stability with 5% weight loss temperatures reaching up to  $550^\circ\text{C}$ . Such superior performance is attributed to the introduced polycyclic arenes end-groups, which lead to stronger conjugation intensity, better hole-transport ability, and higher charge separation stability (Scheme 30).

Ueda and Chen [205,242] reported three series of coPIs, **P31**, **P78**, and **P79** by altering the feeding ratio of electron-accepting moieties, perylenetetracarboxydiimide (PTI), naphthalenetetracarboxydiimide (NTI), and benzenetetracarboxydiimide (BTI), respectively (Scheme 31). The electrical bistability of Al/PI/ITO sandwiched memory devices can be tuned from the volatile to nonvolatile memory behavior by increasing the composition of PTI, NTI, or BTI. Summarizing the results, the conjugation and the electron accepting effects on the resulting memory properties followed the order  $\text{PTI} > \text{NTI} > \text{BTI}$ . The NTI and PTI groups with high electron affinity and long conjugation can stabilize the radical anion, resulting in a stable CT complex and nonvolatile WORM memory properties. On the other hand, the large energy barrier from the Al electrode to the polymer that preventing hole-injection process was produced by the low highest occupied molecular orbital (HOMO) energy level of the BTI unit, leads to the insulator property at a high BTI composition. This work also demonstrated that the composition of the electron-accepting moiety with different conjugation length significantly affected the memory characteristics of D-A coPIs.

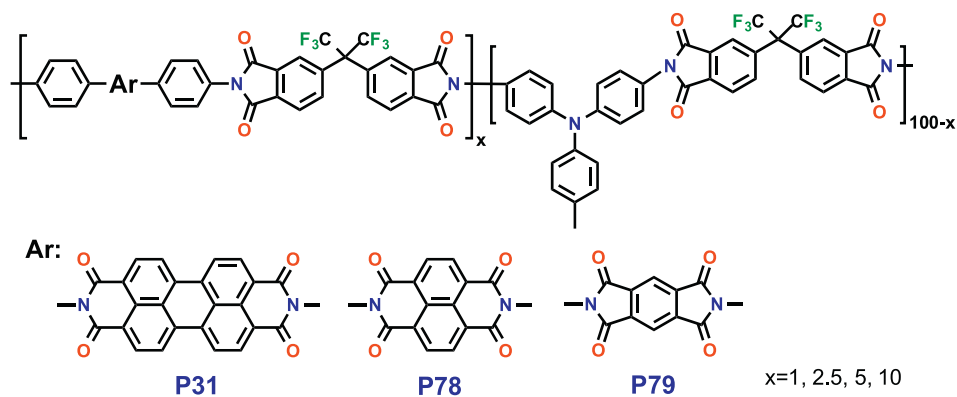
The different dipole moment, HOMO and LUMO energy levels attributed from the PIs **P29** reported by our group recently [198] significantly influence the memory behaviors. The memory devices based on PIs **P29-DSPI** and **P29-NTPI** (ITO/PI/Al sandwiched) exhibit non-volatile WORM memory properties with high ON/OFF current ratio. **P29-DSPI** with a high dipole moment (5.45 Debye) showed WORM memory property, the same as **P29-NTPI**, possessing strong CT effect and low LUMO energy level. On the other hand, memory devices based on PIs **P29-6FPI** and **P29-PMPI** with reduced electron-withdrawing capability, attributed from their corresponding phthalimide units, showed DRAM and SRAM memory properties, respectively. The results showed that the electron accepting capability could influence the polarity, energy level of PIs, and therefore influence the memory performances significantly.

#### 3.4.3. Linkage effect

The Liou group prepared three aromatic PIs (**P80**, **P27** and **P81**) [203,243] based on TPA groups, with pendent anthraquinone attached to the backbone as an electron acceptor, either directly (1-



Scheme 30. Molecular design on the volatility through acceptor effect.



Scheme 31. Molecular design on the volatility through acceptor effect.

and 2-substituted) or incorporated via ether linkage. The PIs were used for the comparison of memory behavior (Scheme 32). All the PIs exhibited excellent thermal stability and high glass transition temperature. The memory devices with configuration of ITO/**P80**/Al exhibited distinct volatile memory characteristics of DRAM while the ITO/**P81**/Al showed volatile SRAM memory property. Thus, the results indicated that the isolated D-A system could effectively extend the retention time in the memory device. On the other hand, the memory device with the configuration of ITO/**P27**/Al exhibited a WORM memory characteristic, showing that the conformational change from steric hindrance can effectively extend the retention time and memory behavior by replacing the substituted anthraquinone from the  $\beta$ - to the  $\alpha$ -position. The ON/OFF current ratios of these memory devices are up to  $10^9$ . The theoretical results suggest that the CT mechanism could be used to explain the memory characteristics of these PIs, and the linkage and steric hindrance effects between the donor and acceptor were also demonstrated.

Another structural effect was clarified by using 6FDA-based PIs **P82** and **P83** [244] prepared from *N*-(2,4-diaminophenyl)-*N,N*-diphenylamine and *N*-(4-(2',4'-diaminophenoxy)phenyl)-*N,N*-diphenylamine, respectively (Scheme 32). Because of the bulky unit, the **P83**-based memory device revealed a more stable non-volatile flash memory characteristic than **P82**-based one with a volatile behavior, supported by a density functional theory-based theoretical simulation. The results also suggested that the higher twisted and isolated conformation between the donor and acceptor unit in **P83** as well as the great distinct charge separation between

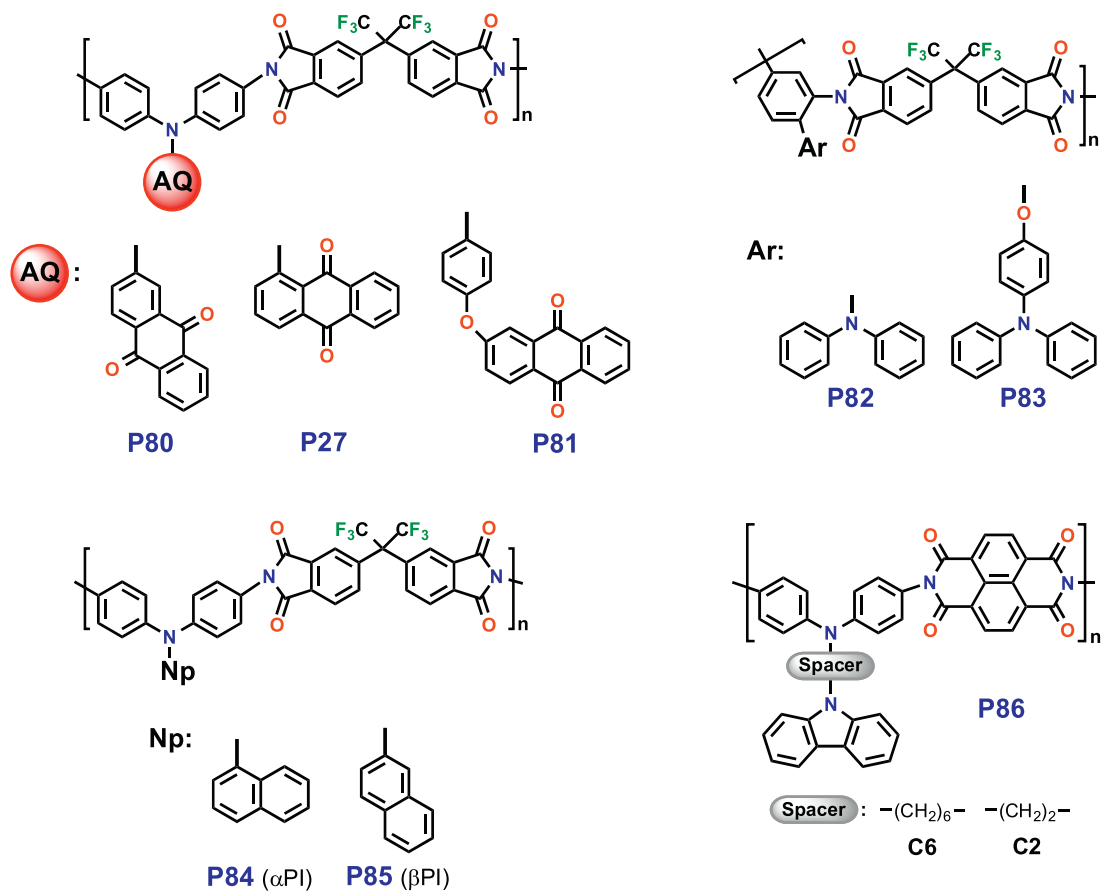
the ground and CT states result in a highly stable non-volatile memory characteristic.

Two functional aromatic PIs, **P84** ( $\alpha$ PI) and **P85** ( $\beta$ PI), based on diphenyl-naphthylamine groups were prepared and by the Qi group and used for memory devices [245], showing the tunable memory properties from the irreversible WORM type (**P84**) to the programmable flash type (**P85**) by altering the position of naphthyl group. **P84** and **P85**-based memory devices (ITO/PI/Au) revealed bi-directionally switched and reprogrammable memory behavior, respectively, with high ON/OFF current ratios. That suggests that the electric-field-induced D-A electronic transition and the subsequent formation of CT complexes could explain the electrical switching effects observed in the synthesized PIs.

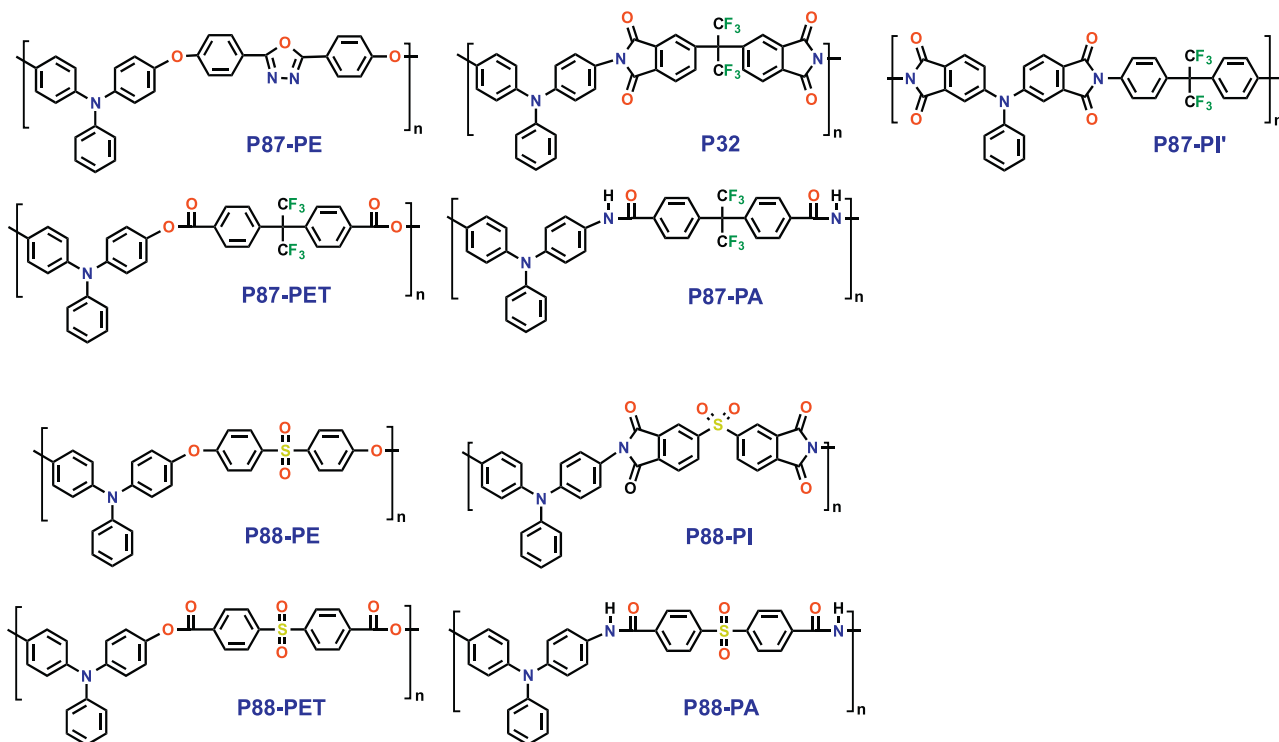
The non-coplanar conformation induced by the diphenyl-naphthylamine in **P84** results in a higher energy barrier than the corresponding conformation in **P85**, thus preventing the back CT processes in the ON state, consistent with a theoretical analysis.

Furthermore, the ethyl and hexyl spacers were inserted into the diamines to alter the spatial position of the electron donor in the PIs **P86**, to elucidate the effect on the memory behavior [246]. Experimental results show that **P86-C6** and **P86-C2** exhibit volatile SRAM and DRAM behavior, respectively. Simulation results indicate that spatial position effect was observed in **P86** with varied length as spacer between carbazole and diphenylamino groups, resulting in different retention time and corresponding SRAM and DRAM behaviors.

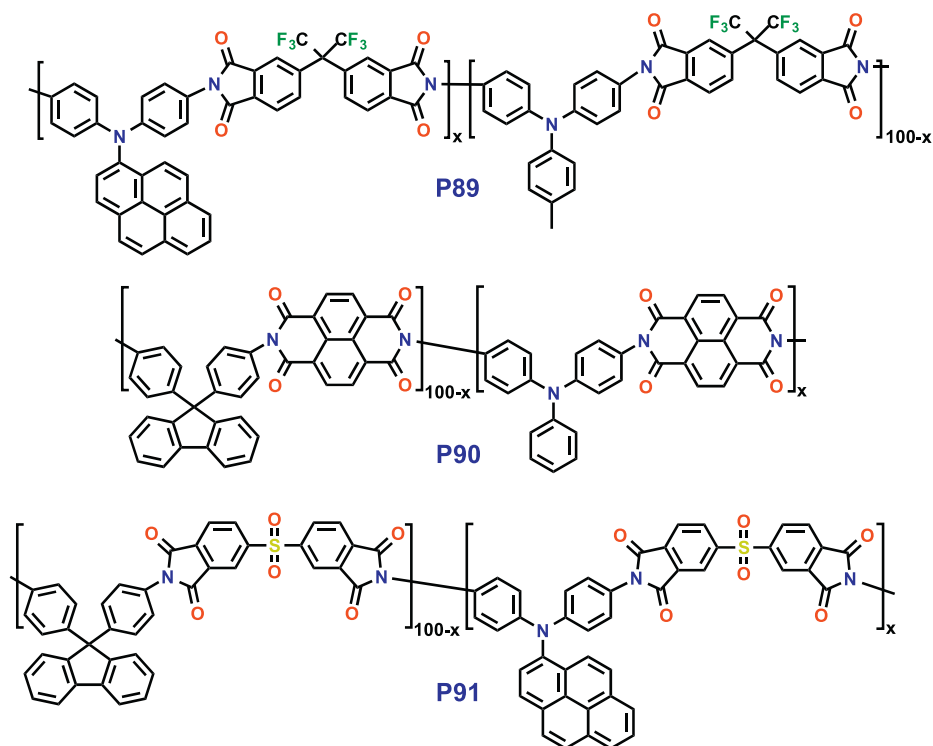




Scheme 32. Molecular design on the volatility through linkage effect.



Scheme 33. Molecular design on the volatility through linkage effect.



**Scheme 34.** Molecular design on the volatility through compositional effect.

PA **P24** with nonplanar linkage and higher dipole moment reveals SRAM property, while **P23** possesses DRAM behavior with high ON/OFF current ratio and excellent stability [201]. In addition, TPA-based aromatic polyether **P87-PE**, polyester **P87-PET**, **P87-PA**, **P32**, and **P87-PI'** were prepared to systematically investigate the relationship between chemical structure and memory behavior (Scheme 33) [247]. The SRAM properties generated from **P87-PE**, **P87-PET**, and **P87-PA** were due to the non-planar linkage structures and different LUMO energy levels. Besides, **P32**-based memory device revealed DRAM property, but its isomer **P87-PI'** exhibits insulator behavior because of the difficulty in sustaining a CT complex. According to the higher dipole moment and conformation effect, 6FPA revealed a longer retention time than 6FPI due to the non-planar amide linkage, which may block the back CT occurring, and the higher dipole moment of 6FPA also could facilitate and stabilize the CT complex. Basically, polymers having isolated and flexible linkages, higher dipole moments, and lower LUMO energy levels will stabilize the CT complex and increase the retention time of polymer memory devices.

Another series of TPA-based sulfonyl-containing aromatic polymers, **P88-PE**, **P88-PI**, **P88-PET**, and **P88-PA**, were synthesized and applied for memory devices fabrication [248]. By choosing the suitable linkage between electron donor and acceptor moieties, tunable memory behavior from insulator (**P88-PE**) to SRAM (**P88-PET**, **P88-PA**, and **P88-PI**) with different retention times could be achieved.

#### 3.4.4. Compositional effect

Ueda and Chen et al. [215] reported flexible, resistance memory devices [poly(ethylene 2,6-naphthalate)/Al/**P89**/Al] using new coPIs **P89** with 6FDA acceptor, and series of randomly copolymerized TPA/pyrene moieties modified by chemical imidization (Scheme 34). The molar percentage content of *N,N*-bis(4-aminophenyl)aminopyrene in the TPA component varied from 0, 5, 10 to 100 (with the corresponding PIs identified as **P89-0**, **P89-5**, **P89-10**, and **P89-100**, respectively). The memory properties vary from volatile to nonvolatile flash, flash/WORM, and WORM mem-

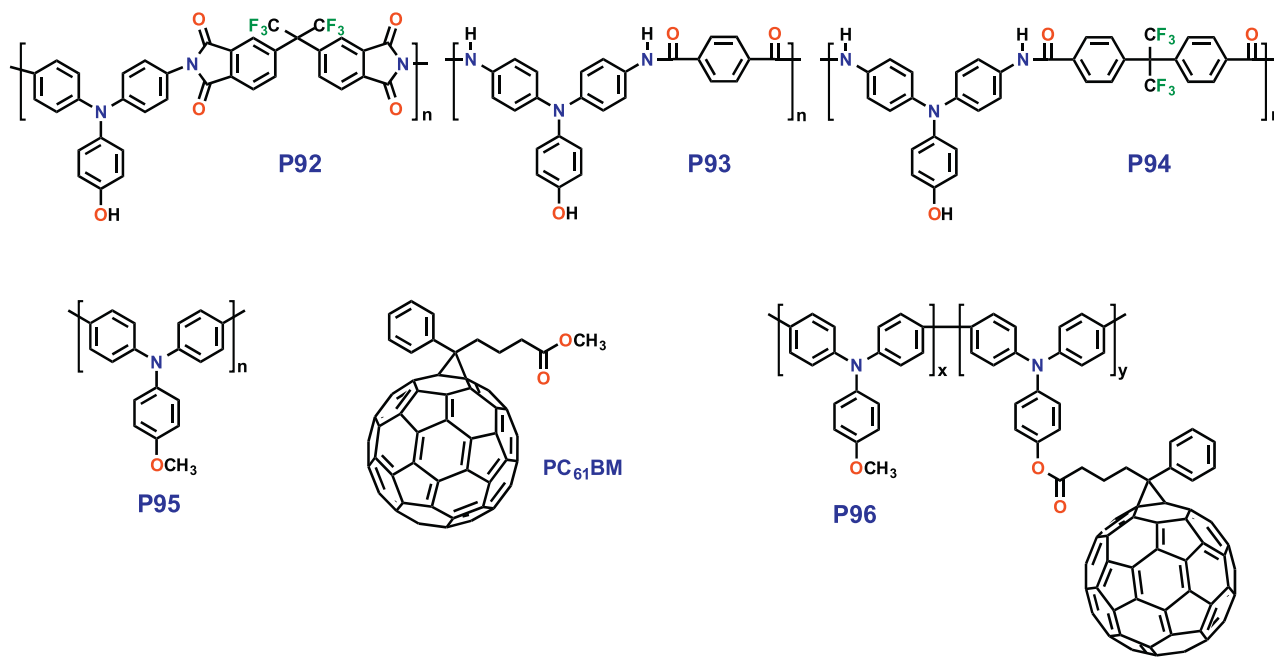
ory performances with the content of the modified TPA. The largely conjugated pyrene units benefit the stable CT complex with excellent nonvolatile electrical properties, as suggested by theoretical simulation.

Qi et al. designed and synthesized copolynaphthalimides (**P90**) [249] and coPIs (**P91**) [250] based on 4,4'-(9-fluorenylidene)dianiline, 4,4'-diaminopyrene, or *N,N*-bis(4-aminophenyl)aminopyrene. Electrical characterization on the ITO/**P90**/Al sandwich devices showed a range of the memory behavior, from no electrical bistability (NULL, **P90-0** and **P90-1**), to SRAM (**P90-2** and **P90-5**), WORM (**P90-10**), demonstrating the importance of composition control on determining memory characteristics. The trend of the memory effect is attributed to the effects of the electron-donating TPA species promote the formation of stable CT complexes. On the other hand, **P91** also exhibits tunable electrical switching behaviors from WORM (**P91-100**, **P91-50**, **P91-20**, **P91-10**) to SRAM (**P91-5**, **P91-1**) with variation of the diphenylaminopyrene content. Optical and electrochemical characterization show gradually decreased HOMO levels and enlarged energy gap with decreased diphenylaminopyrene moiety, suggesting decreasing CT effect in the coPIs can account for the observed WORM-SRAM memory conversion.

#### 3.4.5. Thickness effect

The effect of film thickness on the memory properties of **P6-6FDA** was reported by Lee et al [251]. The results demonstrated WORM memory behavior for thicknesses in the range of 34–74 nm, but that only DRAM memory behavior obtained for a the film thickness increased to 100 nm. The resultant DRAM memory behavior is due to the prevention of stable local filament formation in the thick film.

**P87-PE** reported by our group [247] exhibited insulator, SRAM (with retention time 2 min and threshold voltage 5.6 V), and SRAM (with retention time 2 min and threshold voltage 3.8 V) properties with the corresponding thickness around 50, 40, and 30 nm, respectively. In addition, these aromatic polymers based on TPA



**Scheme 35.** Chemical structures of HPP/PC<sub>61</sub>BM hybrid materials for memory device applications.

groups revealed diverse memory behaviors with high ON/OFF current ratios.

#### 3.4.6. HPP/PC<sub>61</sub>BM hybrids

In addition to various devices based on a single-polymer, hybrid systems have also been extensively reported for memory device applications. Fullerene derivatives serve as supplementary compounds that could be considered as the data storage media or to possess physical electronic transition with the organic polymer matrix.

Liou and coworkers reported three high ON/OFF ratio ( $\sim 10^9$ ) memory devices based on hydroxy-triphenylamine-, OHTPA-, based HPPs with various amounts of electron-acceptor [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) (Scheme 35) [252]. Non-conjugate OHTPA-based polymers are not only advantageous in increasing the ON/OFF ratio due to their low OFF current but are also expected to have a strong interaction with PC<sub>61</sub>BM, resulting in good dispersion and stable memory properties, even at a high PC<sub>61</sub>BM content. Memory devices based on the high-performance polymers, **P92**, **P93**, and **P94** exhibited DRAM, insulator, and SRAM memory properties, respectively. By blending PC<sub>61</sub>BM with lower than 1 wt% into these OHTPA-based polymers, memory behavior of the corresponding devices could be effectively tuned in a wide range from insulator through DRAM, SRAM to WORM. These results demonstrate that the polymer memory characteristics can be effectively manipulated through the structural design of the electron-donating matrix and the incorporation of the electron-acceptor PC<sub>61</sub>BM.

Hybrid materials prepared by blending the thermally stable **P95** with electron acceptor PC<sub>61</sub>BM [253] were also systematically investigated. Memory devices with the configuration of ITO/PC<sub>61</sub>BM:**P95**/Al revealed both DRAM and WORM properties, controlled by the fraction of PC<sub>61</sub>BM. The strong interaction between PC<sub>61</sub>BM and TPA results in well-dispersed PC<sub>61</sub>BM clusters within PC<sub>61</sub>BM:**P95** hybrid films and bistable WORM behavior even with PC<sub>61</sub>BM content up to 10 wt%.

Nonvolatile memory devices containing polyTPA and different amounts of pendent PC<sub>61</sub>BM were also reported by our group and exhibited high ON/OFF ratio [254]. By introducing 10 wt% PC<sub>61</sub>BM

into **P96** via covalent bonding, a WORM memory device with much higher ON/OFF ratio ( $10^9$ ) and lower switching-ON voltage (0.9 V) than that obtained by blending composites has been achieved. Besides, the nonvolatile memory property remained even after heating treatment at 100 °C for 1 h. This result is crucial for retaining stability of device in computer applications when other components produce heat.

#### 3.5. Flexible HPP electrical memory devices

Similar to other organic electronics, the flexible polymer memory device has also been demonstrated using PI as an active layer [204,215,255]. Ueda and his coworkers reported the fabrication of flexible memory devices using poly(ethylene terephthalate) as a flexible substrate [215]. The device showed a very stable nonvolatile behavior even after bending from flat to a radius curvature of 5 mm up to 1000 bending cycles.

Liou and coworkers also reported severe tests of flexible memory devices by bending at various curvature radii [255]. The result shows that the flexible device were not only is free of crack and deformation, but also demonstrated reliable and reproducible memory switching property, even under mechanical bending stress. Like other organic electronics, the development of fabricating memory device into practical application has been carried out, and further optimization should be investigated as guidance for future potential applications.

### 4. Triphenylamine-based materials for electrofluorochromic devices

#### 4.1. Principle/Mechanism

Molecules with fluorescence that can be switched by external stimuli have garnered attention for applications in analytical chemistry, molecular devices, display technology and single molecule detection. Although such molecules have been studied for long time, the term “electrofluorochromism (EFC)”, which deals with the electrically driven reversible optical changes in the fluorescence, has been coined only recently [256–269]. Compared with

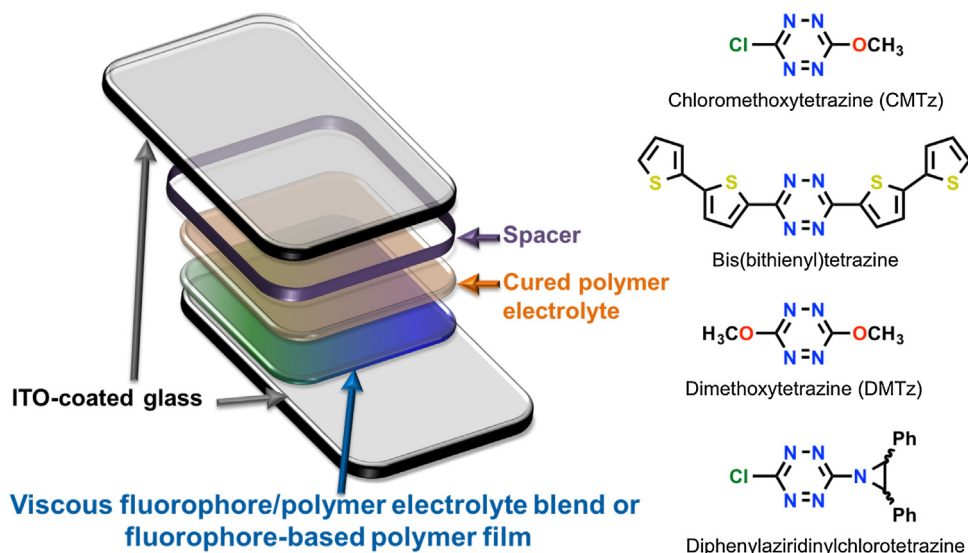


Fig. 11. The first example of electrofluorochromic device.

EC [270] or electrochemiluminescence [271], research in EFC is at a relative early stage. The EFC materials reviewed here may be grouped into the use of small molecules or polymers, with a focus on molecular structures. Small molecules, whose emission is electro-switchable, can serve as dyads or fluorophores with separate redox and fluorescent units. The first such bifunctional fluorescent molecular switches were synthesized by Lehn in 1993 [272], who used a quinone redox state to switch a ruthenium-bipyridine complex on and off. Subsequently, several EFC devices containing small organic molecules [257,273–275], inorganic materials [276–278], conjugated polymers [279,280], HPPs [67,262], and composites [281] have been synthesized and investigated.

The EFC behavior is attributed to three kinds of mechanism, (1) by enabling or forbidding proton or electron transfer between the redox-active unit and luminophore, (2) through the energy transfer resulting from the overlap between absorption of the redox part and emission of the luminophore that controlled by redox reactions, and (3) by directly tuning the electroactive luminophore with its redox states [256].

Dyads or triads with a redox moiety and luminophore moieties, directly conjugated/non-conjugated linked or through a bridge, are used as models for two mechanisms. The redox moiety with luminophore exhibits emission changes during the electrochemical reactions. The critical issue for developing new EFC systems is the proper match of the redox unit and electroactive luminophores. Although most ionic radicals and dications or dianions are neither stable nor luminescent, a few stable anion- and cation-radicals comprising of the counterparts, such as triaryl amines [67] and tetrazines [282], have been developed and investigated as promising emissive materials.

#### 4.2. Electroswitchable fluorophores

Audebert and Kim et al. first reported devices composed of a tetrazine/polymer electrolyte blend and proved the possibility of *in-situ* operated fluorescent device during electrochemical switching (Fig. 11) [274]. The configuration of EFC devices is generally the same as traditional EC devices. Two-electrode and three-electrode devices are two main multilayered structures of EFC devices, which differ from whether inserting a silver wire as reference electrode or not. A three-electrode device provides tunable electrical conversion, when compared with two-electrode, and is beneficial for multicolor switching devices [256]. Both devices are composed of

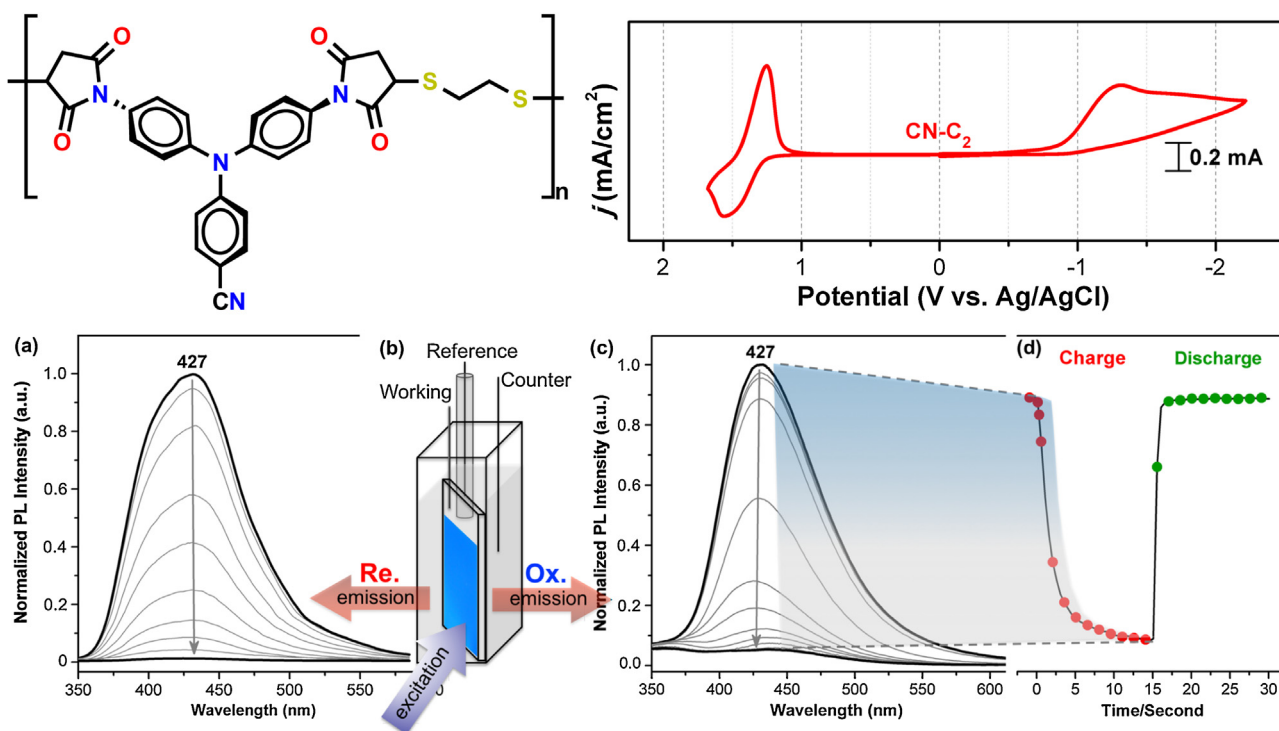
the same configuration (Fig. 11), including EFC-active materials, transparent electrodes (i.e., working and counter electrodes), and electrolyte. Moreover, the complementary EFC layer is usually a second electroactive component and used as the counter electrode. During the time voltage is applied between the electrodes, the luminescence of the EFC films may be tuned as the electrode ions are extracted from or doped into the EFC films [283] (Fig. 12). Therefore, the capability of transporting both electron/ion and the completion of a circuit with high ion conductivity is an essential requirement for EFC layers [284]. The second electroactive layer with a charge balance ability was beneficial factor to EFC performance in terms of optical contrasts, operational voltages, response time, emission efficiency, and cyclability [285–287]. For example, Prussian blue or HV is one of the most frequently used complementary materials for EFC devices. After that surprising study, many related publications have risen and the reported materials can be generally categorized into small molecules and polymeric materials as discussed in the following.

##### 4.2.1. Small molecules

4.2.1.1. *Quinones*. Quinones are the most well-known organic electroactive group used in dyads, and the representative component benzoquinone may be reduced to hydroquinone with two electrons and two protons required. The first EFC molecule **M1** consisted of a fluorescent  $\text{Ru}(\text{bpy})_2^{2+}$ -moiety attached to a quinone (Scheme 36) [272]. Since the quinone quenches the triplet state of  $\text{Ru}(\text{bpy})_2^{2+}$ , reduction to the hydroquinone restores fluorescence.

4.2.1.2. *Tetrathiafulvalenes*. Tetrathiafulvalenes constitute another well-known electroactive group. They are often employed in molecular and supramolecular switches due to their favorable properties, including stable and reversible electrochemical behavior. The non-aromatic molecule **M2** may be oxidized into a radical cation and subsequent dication, which are stable and reversible in redox reactions due to the increasing aromaticity [273].

4.2.1.3. *Thienoviologen*. Beneduci et al. first demonstrated the preparation of EFC ionic liquid crystal, thienoviologen **M3**, which was derived from the typical EC chromophore viologen [288]. Besides an unordered isotropic phase, two ordered phases could be formed (columnar and calamitic). Fluorescence was observed upon reduction as the radical is formed. For the isotropic phase the increasing fluorescence is accompanied by a redshift in emission,



**Fig. 12.** Cyclic voltammetric diagrams of the polyimidothioether film and (a) fluorescence intensity changes by applying the electric voltage to  $-2.0$  (V vs. Ag/AgCl). (b) Scheme of a typical electrofluorochromic cell (c) fluorescence intensity changes, and (d) monitored switching behavior by increasing the applied voltage to  $1.70$  (V vs. Ag/AgCl). [268], Copyright 2018. Reproduced with permission from the Royal Society of Chemistry.

which attributed to the isotropic phase converting into an ordered phase at reduction form. Because of the acceptor-donor acceptor (A-D-A) feature and extended  $\pi$ -conjugation, the incorporated oligothiophene revealed relatively high PL [289]. As bipyridinium salts, thienoviologens are strong electron acceptors, which exhibit two reduction steps upon continuously decreasing negative potential. Recently, Beneduci et al. also gave the molecular mechanistic hypothesis [290] and demonstrated the EFC characteristics render the strong electron acceptors thienoviologens, exhibiting two reduction couples, as promising candidates for EFC applications.

**4.2.1.4. Tetrazines.** Small molecular tetrazines may be used as electroswitchable fluorophores on their own [274,291]. However, tetrazines generally have weak absorption coefficients of around  $500\text{--}1000\text{ mol}^{-1}\text{ L cm}^{-1}$ , resulting in restricted switching contrast and fluorescence intensity [292]. The Audebert group incorporated TPAs as electroactive groups within tetrazine to generate bichromophores **M4** [293]. Whereas fluorescence could be restored on oxidation, due to spectral overlap the quantum yield was low [294]. To resolve this issue, TPA moieties with electron-rich groups were investigated [295]. These groups shift the absorption of the cationic TPA radical to a higher wavelength, thus preventing spectral overlap. In another example, with naphthalimide attached tetrazine fluorophore, the dyad absorbed light efficiently, exhibited a longer lifetime and stronger fluorescence than the single tetrazine because of the quasi-complete energy transfer [296].

**4.2.1.5. TPA-based molecules.** Alain-Rizzo et al. [7,297] reported the study of the chemical and EFC properties of systematically synthesized TPA derivatives **M5**. TPA-based molecules were characterized by cyclic voltammetry, UV-vis and fluorescence spectroscopy. Theoretical calculations were also performed in order to corroborate the experimental results. This fluorescent switching may be achieved for both electro-donating and electro-withdrawing substituted TPA, but the use of donor group is recommended for the

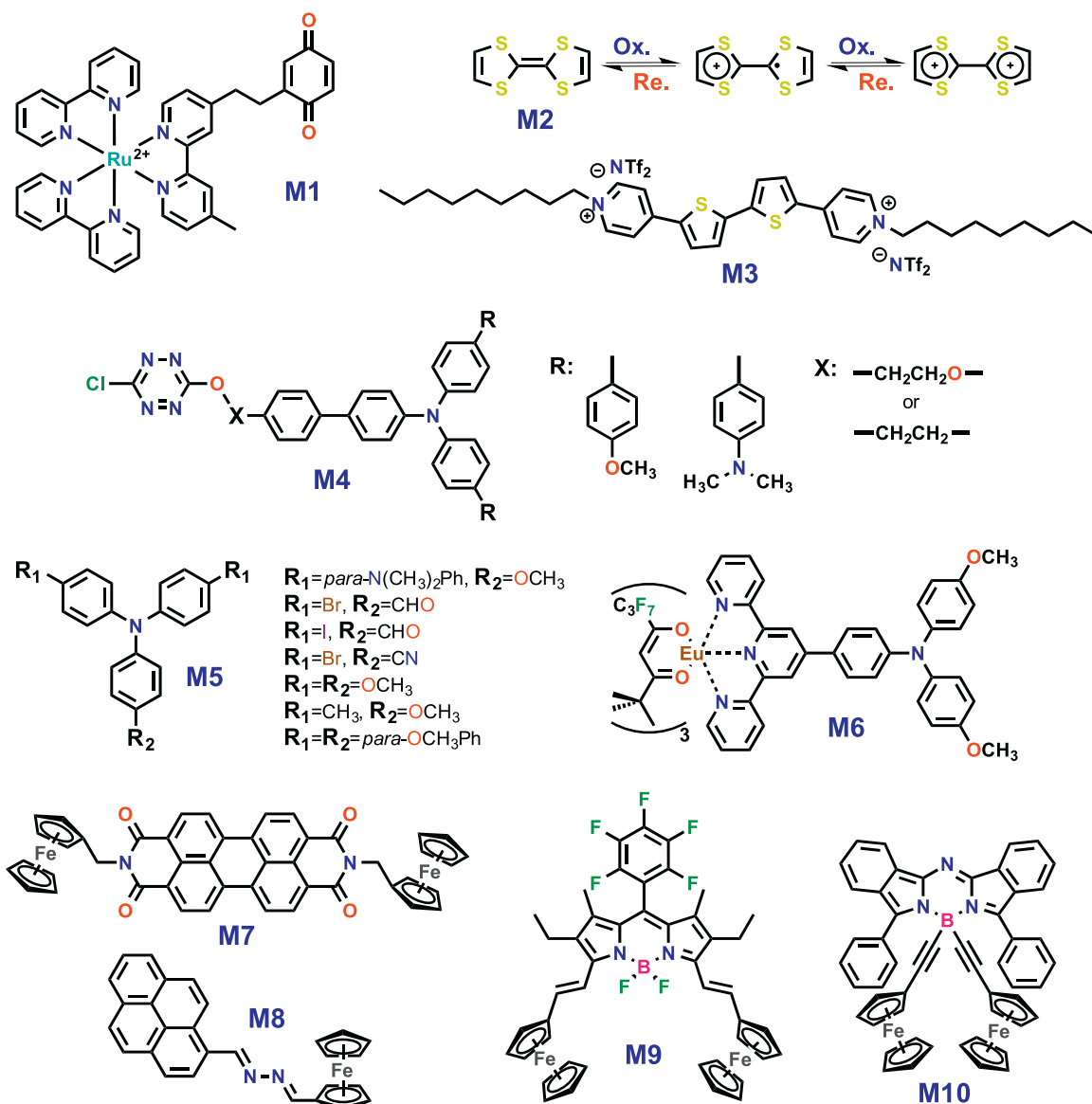
fabrication of EFC devices since the radical-cation is more stable. The fluorescence behavior may be switched between the strong fluorescent (neutral) state and the nonfluorescent (oxidized) state with a contrast of more than a thousand-fold, which is significant for practical EFC applications.

**4.2.1.6. Metal coordination.** Lanthanide complexes are another classic luminophores with favorable properties, such as a long luminescent lifetime, large Stokes shift, and a narrow emission band. Thus they can be combined with electroactive units to generate EFC molecules. The europium (Eu) complex **M6** reported by Yano et al. was prepared by directly coordinating TPA-linked terpyridine ligand to Eu tris( $\beta$ -diketonate) [298]. The results showed that the luminescence from  $\text{Eu}^{3+}$  was switched reversibly due to the intramolecular energy transfer from complexes to TPA radical cation.

By coupling another redox-active Fc with luminescent substituents through conjugated bridges, the triads could demonstrate photoinduced electron transfer (PET) or intramolecular CT in the neutral form, and would be restricted at their redox state thus switches emission behavior [299]. For example, Zhang et al. prepared a triad **M7** containing Fc and fluorescent perylene diimide [300]. During the electrochemical oxidation and reduction, the fluorescence of **M7** was turned on and off reversibly due to the released and suppressed PET process. Similarly, the EFC-active triad **M8** reported by the Martínez group was prepared by bridging Fc and pyrene with azine [259]. By increasing the applied potential to oxidized Fc, the fluorescence of the triad was turned on, and the fluorescence intensity could be further turned off by lowering the applied potential to its neutral state, due to the recovered ET from Fc to pyrene.

Different from the above Fc based EFC molecules depending on the PET effect, a boron dipyrromethene dye was used by attaching Fc either to its two side-rings [301,302] or the boron atom [302]. It was found that attachment to boron promoted intersystem cross-





**Scheme 36.** Chemical structures of some EFC small molecules.

ing from singlet to triplet state, a phenomena often associated with the presence of heavy atoms. This crossing allowed the excited state lifetime of the dyad to be extended by three orders of magnitude. These Fc-type triads **M9** and **M10** are intriguing for the uses in molecular probes and sensors of redox processes.

#### 4.2.2. Polymer materials

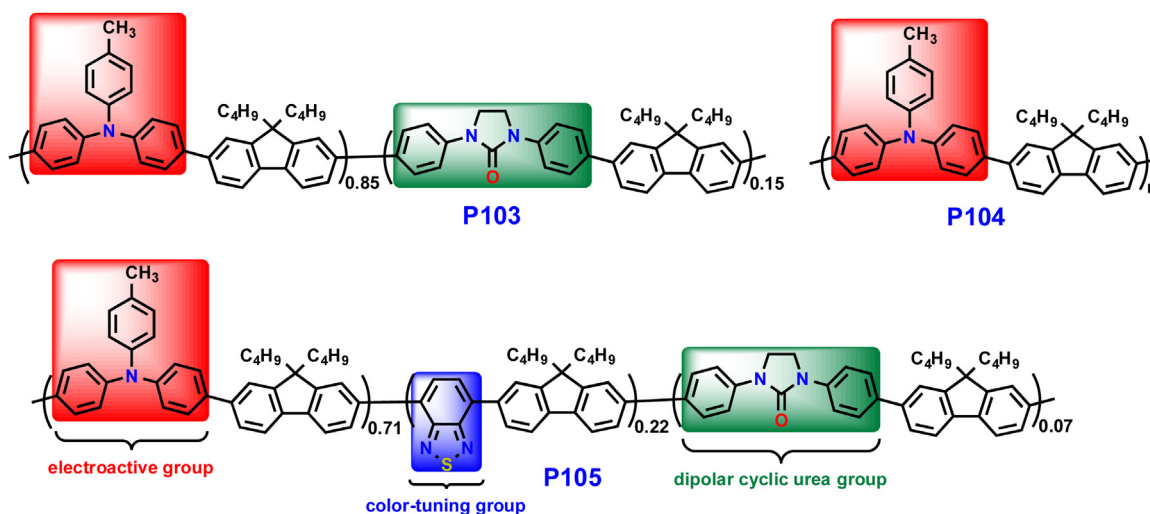
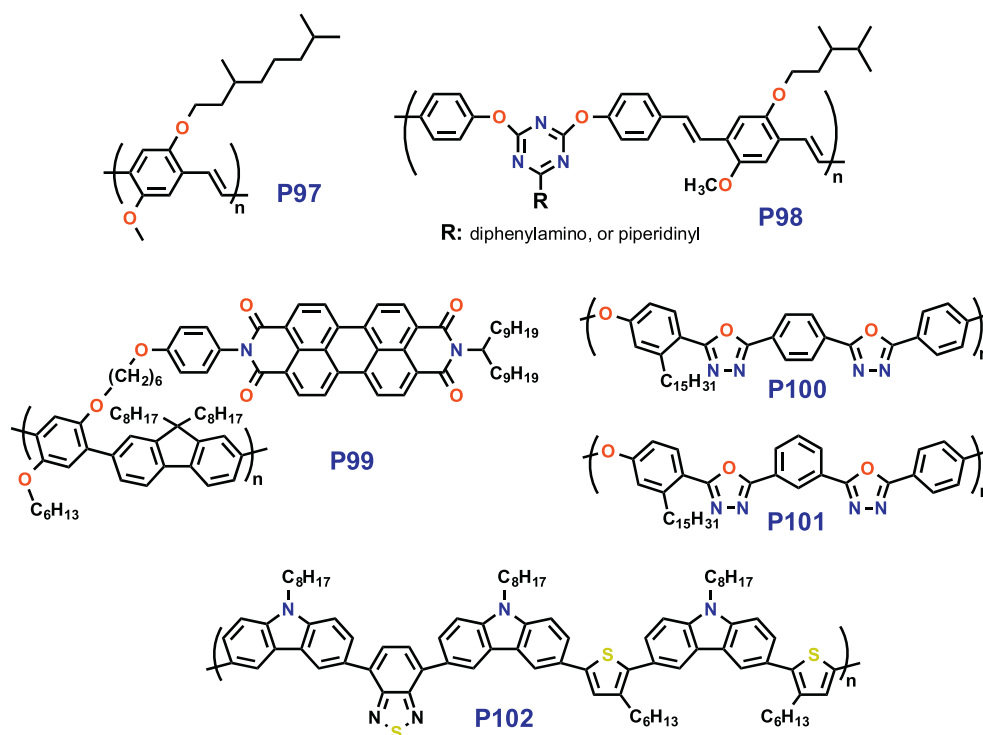
**4.2.2.1. Poly(phenylene-vinylene)s.** Poly(phenylene-vinylene)s have been extensively applied as photovoltaic cells and organic light-emitting diodes, and were also reported recently could be used as EFC devices [303]. For example, the fluorescence deactivation of **P97** reported by the Montilla group was studied by in situ electrochemical fluorescence spectroscopy during p-doped scanning (Scheme 37) [304]. The critical points, such as electrolyte diffusion, processes of electrochemical doping, and degradation processes, were extensively investigated to understand the EFC processes.

More researches have done on several EFCs based on poly(phenylene-vinylene)s derivatives. The triazine bridged poly(phenylene-vinylene)s **P98** were reported to exhibit multi-state fluorescence switching that induced by iodide ions [258].

Polymer electrolyte layer and **P98**-doped gel layer were applied to fabricate the solid state two-electrode device an iodide and iodine couple, and the fluorescent intensity resulting from redox reactions of iodine dopants was strongly dependent on the applied potential.

**4.2.2.2. Conjugated polymers.** The emission color of  $\pi$ -conjugated D-A polymers can be tuned over a wide range by incorporating electron-donating and accepting moieties into polymer backbone [305]. The rapid transport of excitons along the  $\pi$ -conjugation chain and high degree of  $\pi$ -delocalization result in the sensitivity of fluorescent responses [280].

For example, Montilla et al. reported a fluorene-*alt*-phenylene copolymer **P99** with an electron-accepting PTI pendant unit, and its photoluminescence was largely suppressed upon electrochemical oxidation due to the photoinduced electron transfer from conjugated chain to neutral PTI aggregates [275]. The fluorescence was then recovered upon the reduction because of the inhibited photoinduced electron transfer and the formation of radical anion. When applying more negative potentials, the Förster resonance

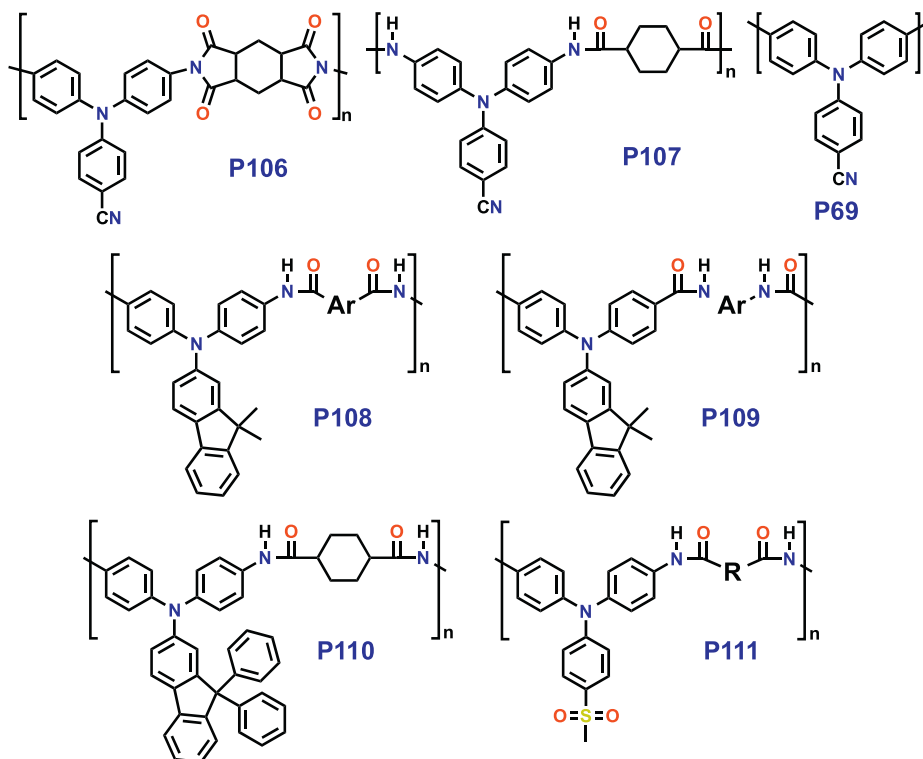


energy transfer to PTI radical dianion occurs, quenching the emission from the conjugated chain.

Basically, polymers with good solubility are capable of facile solution processing. In this regard, fluorescent and solution-processable poly(1,3,4-oxadiazole)s **P100** and **P101** with flexible, long alkyl groups were reported by E. Kim et al., and the derived three-electrode EFC devices were fabricated via spin-coating [262]. The patterned EFC films through photo-cleavage of **P100** displayed reversible EFC behaviors under applied voltage between +1.8 and -1.8 V. During the reduction, **P100** with  $\pi$ -conjugation through C1-C20 exhibited excellent electrochemical reversibility and stability over 1000 cyclic bright/dark switching operation. However, **P101**-based EFC device was not very responsive due to the interrupted  $\pi$ -electron delocalization of its radical.

EFC-active polymers can also be applied to selectively detect ions. For example, Lu et al. demonstrated the use of benzothiadiazole-based conjugated polymer **P102** for EFC detection of cyanide ( $\text{CN}^-$ ) [279]. Since nucleophilic  $\text{CN}^-$  interacted with electron-deficient benzothiadiazole, the oxidative fluorescence quenching was strongly weakened. Such EFC a polymeric sensor can be utilized to quantify ion concentration.

The Leung group reported conjugated copolymers **P103-P105** with fluorene and TPA both in the main-chains [306]. Regarding the structural design, fluorene-based **P104** exhibited high fluorescence and can be switched due to the generated TPA radical cations. During the electrochemical process, **P103** with bipolar cyclic urea unit revealed ion transport. The conjugated polymers showed blue fluorescence with a high quantum yields of ~65% and 40% in solu-



**Scheme 39.** Chemical structures of EFC TPA-based polymers.

tions and thin film states, respectively, which could be quenched reversibly during oxidation steps. Notably, the improved response time of the EFC devices was due to the stabilized radical cations and electrolyte diffusing resulting from cyclic urea. The electron acceptor benzo[2,1,3]thiadiazole segment was introduced into **P105** for fine-tuning the emission color and band gap via intramolecular CT [280]. The resulting thermally stable and organosoluble **P105** emitted yellow light was further utilized to achieve white-light fluorescence by blending with **P103** (blue) according to the energy transfer between them. Thus, the EFC devices derived from **P105** and **P103** have their fluorescence simultaneously quenched upon suitable applied voltage, resulting in a white/dark emitting switching (Scheme 38).

**4.2.2.3. TPA-based polymers.** Flexible EFC devices based on cyanotriphenylamine containing PI **P106** and PA **P107** were prepared, revealing aggregation-enhanced emission properties and remarkable EFC contrast ratio of 151.9 for **P107** (Scheme 39) [67]. The results confirmed that introducing aggregation-enhanced emission-active chromophores is a feasible approach for developing high-performance EFC polymers. However, the response times for partially conjugated **P106** and **P107** were relatively long even with high contrast ratios. Therefore, a high-performance EFC device was fabricated by a fully conjugated **P69** with TPA as building blocks [286]. Thin films of **P69** in the neutral state revealed a strong PL at 470 nm, rapidly quenched at the oxidized state. The EFC device based on fully conjugated **P69** with enhanced charge transport capacity possessing a high contrast ratio of 242 and a rapid response of less than 0.4 s (Fig. 13). On the other hand, the highly efficient luminophore fluorene was incorporated to improve the durability and thermal stability of PA **P108-P111** [76,98,101,102]. An anodic EFC device based on **P108** revealed notable PL intensity with improved EFC cyclic switching stability.

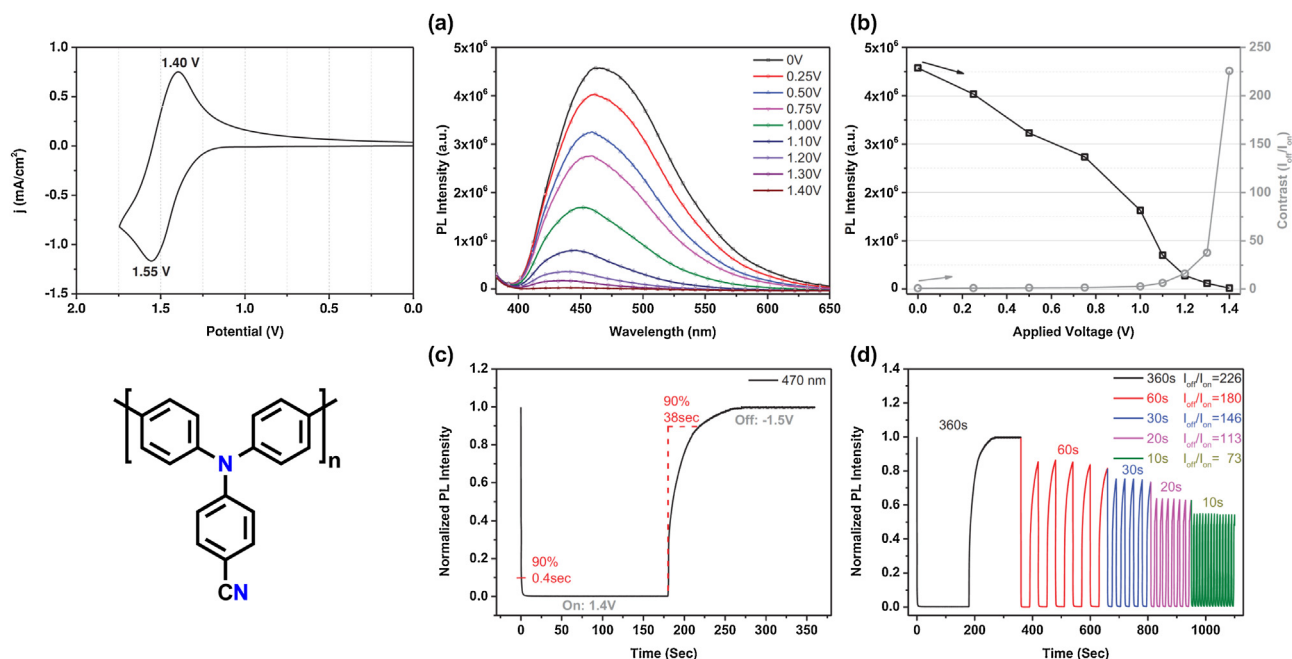
## 5. Conclusions and outlook

Recent development of TPA-based advanced materials for various optoelectronic applications are summarized in the preceding, including EC, EFC, and polymeric memory devices. Over recent decades TPA has been widely used as photoconductors, light-emitters, and especially hole-transporting materials in organic light-emitting diodes, solar cells, organic field-effect transistors and photorefractive materials, attributed to its high electro-activity of the nitrogen center and the ability to transport positive charge efficiently via the radical cation species.

The preceding presents a systemic discussion the structural design, optical and electrical properties of HPPs containing TPA unit, that will provide the scientific community with a greater understanding of recent developments and further prompt the engineering and conceptual design of materials for a number of emerging applications (data storage, displays, and flexible electronics).

TPA-based EC HPPs have attracted increasing attention due to their promising optical and electrical properties that make them with great potential for practical applications. Moreover, the recent development of EC devices derived from HPPs, including the structural design, synthesis, and characteristic evaluation have also been discussed and summarized. Based on the excellent and interesting results of these HPP-derived EC devices, we believe that the optimization could further improve device performance and fully explore the potential of these multicolored EC devices for wearable applications, smart windows in building construction, shutters of aircraft, sunroof and auto-dimming rearview mirror for automobiles, electronic tag and displays.

The development of polymers for use in solution processable fabrication of high mechanical strength, low cost, and high-density data storage memory devices is an emerging area. HPPs are the most attractive materials for memory applications when considering the



**Fig. 13.** Cyclic voltammogram of P69/HV device and (a) PL spectra, (b) applied voltage vs PL intensity and contrast diagram, (c) switching time test, and (d) PL intensity and contrast under multi-cycle scanning at different step cycle time. [286]. Copyright 2014. Reproduced with permission from John Wiley & Sons Inc.

critical issue of heat resistance during the device fabrication process and operation due to their high thermal/dimensional stability and mechanical strength. Nearly the current level of memory performances, may be reproduced by carefully considering the structural design based on the systematically investigated switching mechanisms. The extremely high endurance during long-term operation makes HPP a very promising material for memory applications.

EFC that deals with the electrically driven reversible optical changes of fluorescence has only recently been coined. Research is at a relative early state compared to fields in electrochemical manipulation of optical properties such as EC (redox-switchable color) or electrochemical light generation by electrochemiluminescence. Molecules whose fluorescence can be switched by external stimuli have garnered attention for applications in (bio)analytical chemistry, molecular devices, display technology and single molecule detection. EFC devices containing small organic molecules, inorganic materials, conjugated polymers, HPPs, and composites have been synthesized and investigated.

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