

## Electrochemical Synthesis of Redox-active Poly(arylamine-imide)s from Bis(triphenylamine)-Diimides for Electrochromic Applications

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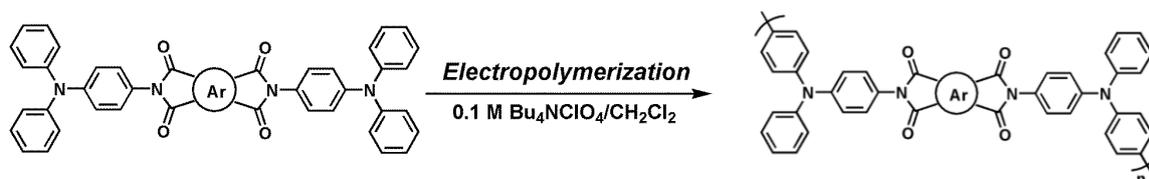
Electrochromism is the phenomenon displayed by an electroactive species that changes color reversibly in response to an applied electrical charge [1]. A vast number of electrochromic materials have been studied, and transition metal oxides, molecular dyes, and  $\pi$ -conjugated polymers are the most frequently investigated components. Some organic-inorganic coordination polymers have also received great interest for electrochromic applications. In general,  $\pi$ -conjugated polymers show several advantages over the other types of electrochromics, such as high coloration efficiency, rapid switching speeds, high optical contrasts, ease of processing, and the possibility to tune the properties through chemical modification. Potential applications of electrochromic materials include optical switching devices, electrochromic displays, sunglasses, antiglare rear-view mirrors, smart windows for cars or buildings, data storage, electronic papers and adaptive camouflage. Recent high-profile commercialization of electrochromics includes the Boeing 787 Dreamliner windows manufactured by Gentex.

Triphenylamine (**TPA**) derivatives and polymers are well-known for their electroactive and photoactive properties that may find optoelectronic applications as photoconductors, hole-transporters, and light-emitters [2,3]. **TPAs** can be easily oxidized to form stable radical cations as long as the *para*-position of the phenyl rings is protected, and the oxidation process is always associated with a strong change of coloration. During the past decade, a huge amount of high-performance polymers (typically, aromatic polyamides and polyimides) carrying the triarylamine unit have been prepared and evaluated for electrochromic applications by Liou's research group [4]. Unsubstituted **TPA** undergoes dimerization to tetraphenylbenzidine (**TPB**) after the formation of an unstable monocation radical [5]. This is accompanied by the loss of two protons per dimer and the dimer is more easily oxidized than TPA and also can undergo further oxidations in two discrete one-electron steps to give  $\text{TPB}^{+\bullet}$  and finally the quinoidal  $\text{TPB}^{+2}$ . Quantitative data have been obtained for several 4-substituted triphenylamines in the form of second-order coupling rate constants, and it was generally found that electron-donating substituents such as methoxy group tended to stabilize the cation radicals while electron-withdrawing groups such as nitro group had the opposite effect. Therefore, it is possible to design electropolymerizable monomers by attaching two or more TPA units to an electron-withdrawing core. Electrochemical polymerization provides the unique advantage to combine both synthesis and direct fabrication of electroactive polymer films on the electrode surface. This procedure significantly shortens the experimental time and avoids the solubility issues often encountered with conventional chemical methods, thus enlarging the scope of candidate polymers for electrochromic applications.

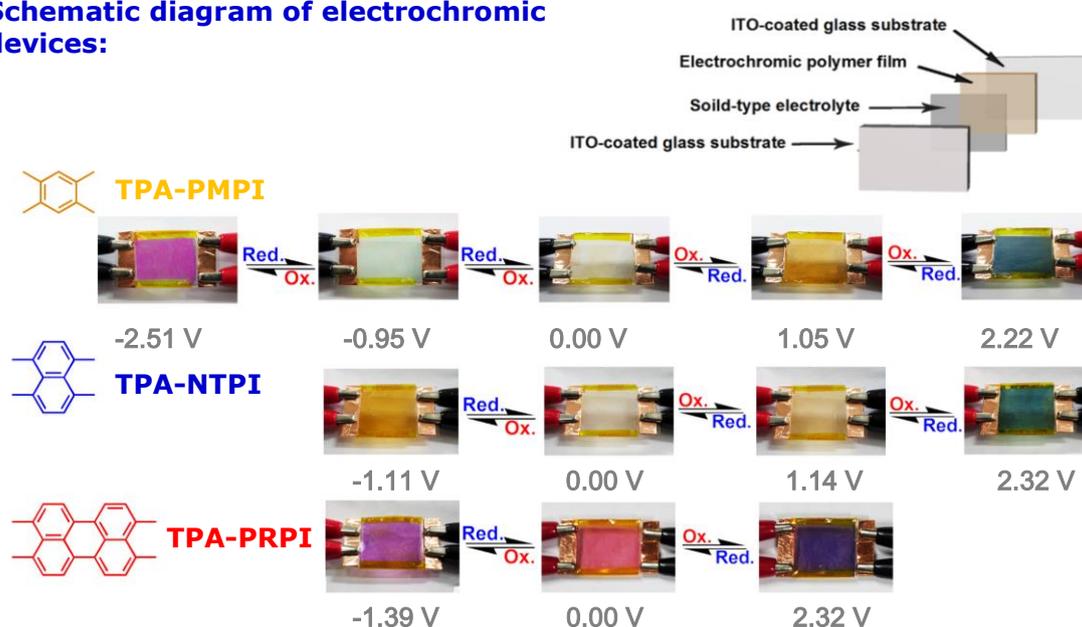
As a continuation of our recent efforts in developing electrochromic materials by electrochemical synthesis [6,7], herein we synthesize three bis(triphenylamine)-diimide compounds, **TPA-PMDI**, **TPA-NTDI** and **TPA-PRDI**, from the condensation reactions of 4-aminotriphenylamine with pyromellitic dianhydride (**PMDA**), 1,4,5,8-naphthalenetetracarboxylic dianhydride (**NTDA**) and 3,4,9,10-perylenetetracarboxylic



dianhydride (**PRDA**), respectively. Redox-active poly(arylamine-imide) films coded as **TPA-PMPI**, **TPA-NTPI**, and **TPA-PRPI** could be electrodeposited robustly on the electrode surface in an electrolyte solution via the oxidative coupling reactions between the TPA radical cations. The cyclic voltammograms of these electrodeposited films showed an ambipolar redox behavior, with a reversible redox couple during the anodic scanning and two pairs of redox waves during cathodic scanning. The polymer films exhibited multicolored electrochromism during both anodic and cathodic scanning. Electrochromic devices using the electropolymerized films as active layers were also fabricated as preliminary investigations for electrochromic applications.



**Schematic diagram of electrochromic devices:**



## References

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