Electrochemical and Electrochromic Properties of Aromatic Polyamides and Polyimides with Phenothiazine-based Multiple Triphenylamine Cores

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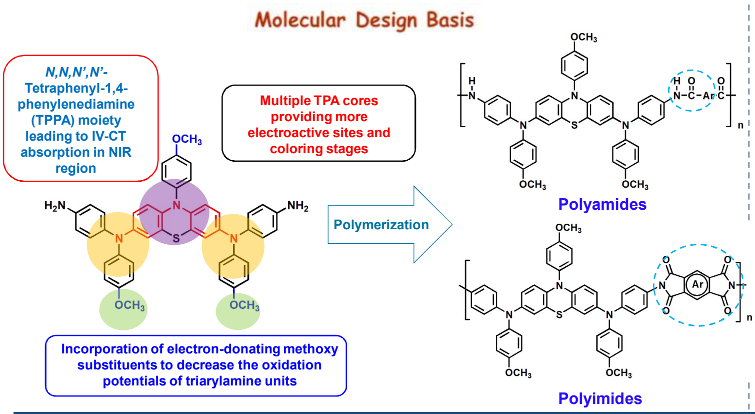
Abstract

A phenothiazine-derived diamine monomer, 3,7-bis[*N*-(4-aminophenyl)-*N*-(4-methoxyphenyl)amino]-10-(4-methoxyphenyl)-10H-phenothiazine (**4**), has been successfully synthesized, leading to the development of new electroactive aromatic polyamides and polyimides. The resulting polymers exhibit excellent solubility in polar organic solvents and can be solution cast into strong, flexible films. These polymers display a distinct pink color change during their first-stage oxidation, transitioning to blue during the second-stage oxidation. Cyclic voltammetry results indicate that the polymers possess two reversible oxidation redox couples, occurring at 0.47–0.61 V and 0.73–0.85 V. Additionally, these polymers demonstrate remarkable electrochemical and electrochromic stability, along with high coloration efficiency and intense absorption in the near-infrared region upon oxidation.

Keywords: Electrochemistry, Electrochromism, Triphenylamine, Phenothiazine, Polyimides, Polyamides

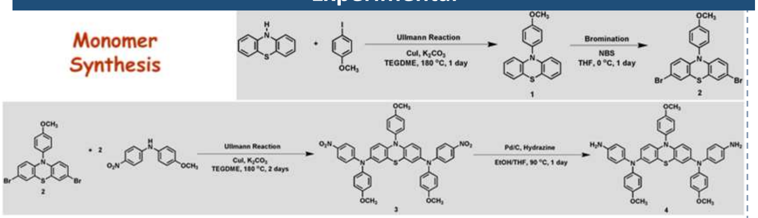
Introduction

Molecular Design Basis



Experimental

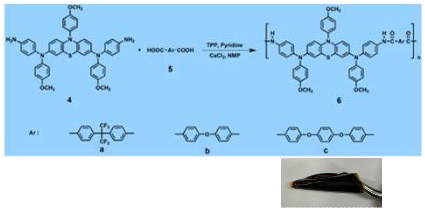
Monomer Synthesis



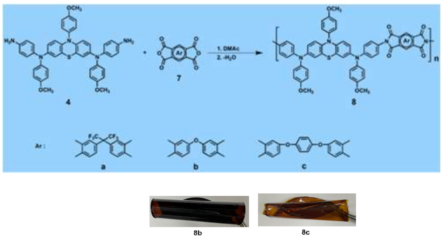
Scheme 1. Synthesis route to 3,7-bis-[4-aminophenyl(4'-methoxyphenyl)amino]-10-(4-methoxyphenyl)phenothiazine (**4**).

Experimental

Polymer Synthesis



Scheme 2. Synthesis of polyamides **6a-6c**.



Scheme 3. Synthesis of polyimides **8a-8c**.

Structural Characterization

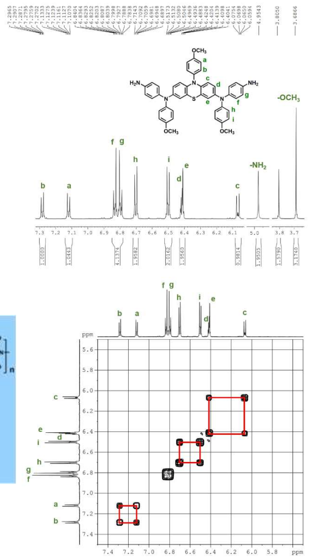


Figure 1. ^{1}H NMR and H-H COSY NMR spectra of the targeted diamine monomer **4** in DMSO-d_6.

Results and Discussion

Electrochemical Properties

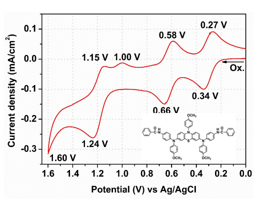


Figure 2. The CV diagram of model compound.

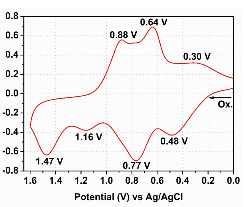


Figure 3. The CV diagram of polyamide **6b**.

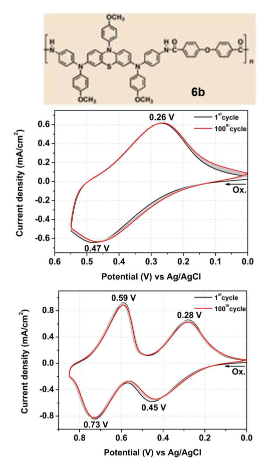


Figure 4. Repetitive CV diagrams of the cast film of polyamide **6b** on ITO-glass substrates in 0.1 M Bu_4NClO_4/MeCN in the ranges of 0.0 – 0.6 V and 0.0 – 0.9 V at a scan rate of 50 mV/s.

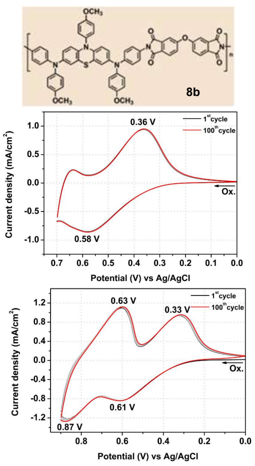


Figure 5. Repetitive CV diagrams of the cast film of polyimide **8b** on ITO-glass substrates in 0.1 M Bu_4NClO_4/MeCN in the ranges of 0.0 – 0.7 V and 0.0 – 0.9 V at a scan rate of 50 mV/s.

Table 1. Redox potentials and energy levels of polymers.

Polymer code	Thin film absorption wavelength (nm)		Oxidation potential (V)[a]			E_g^{opt} (eV)[b]	HOMO (eV)[c]	LUMO (eV)[d]
	λ_{max}	λ_{onset}	E_{onset}	$E_{1/2}^{Ox1}$	$E_{1/2}^{Ox2}$			
6a	310	444	0.26	0.39	0.69	2.79	−4.75	−1.96
6b	309	431	0.23	0.37	0.66	2.88	−4.73	−1.85
6c	309	430	0.28	0.37	0.68	2.88	−4.73	−1.85
8a	309	432	0.32	0.46	0.72	2.87	−4.82	−1.95
8b	311	427	0.34	0.47	0.75	2.90	−4.83	−1.93
8c	309	420	0.34	0.47	0.75	2.95	−4.83	−1.88

[a] vs. Ag/AgCl in CH_3CN. $E_{1/2}$ = average potential of redox couple peaks.
[b] Bandgap calculated from the absorption edge of the polymer film: Energy gap = 1240/λ_{onset}.
[c] The HOMO energy levels were calculated from $E_{1/2}^{Ox1}$ values of CV curves and were referenced to ferrocene (4.8 eV relative to the vacuum energy level), $E_{1/2}$ = 0.44 V.
[d] $E_{HOMO} = -(E_{1/2}^{Ox1} + 4.8 - 0.44)$ (eV); $E_{LUMO} = E_{HOMO} + E_g^{opt}$.

Spectroelectrochemical Properties

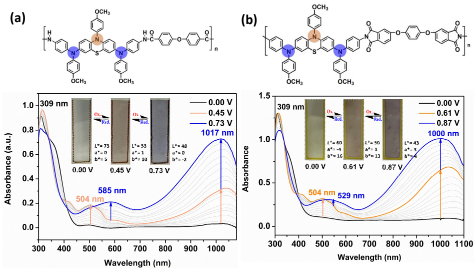


Figure 6. Spectroelectrograms and color changes of the cast films of (a) polyamide **6b** and (b) polyimide **8c** on an ITO-glass slide in 0.1 M Bu_4NClO_4/MeCN at various applied voltages.

Electrochromic Switching Response

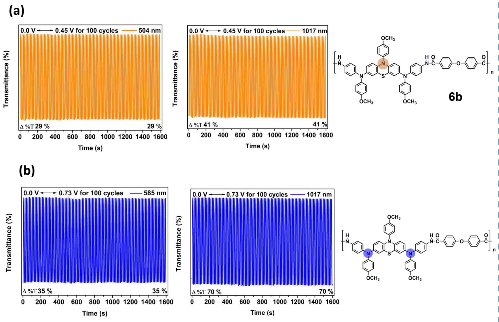


Figure 7. Electrochromic switching responses of the cast film of polyamide **6b** on the ITO-glass slide (coated area ~ 0.8 x 2.2 cm²) in 0.1 M Bu_4NClO_4/MeCN by applying a potential step: (a) potential 0.00 V ⇆ 0.45 V and (b) 0.00 V ⇆ 0.73 V with pulse width of 8 s, monitored at indicated λ_{max}.

Electrochromic Devices

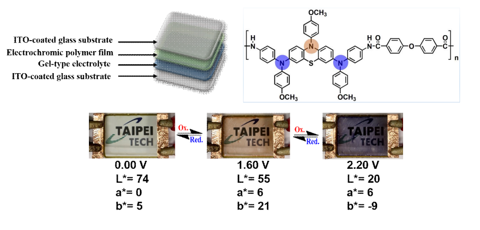


Figure 8. Schematic representation of the electrochromic device and the colors of polyamide **6b** devices at indicated applied potentials.