Multicolor electrochromic poly(amide-imide)s with *N*,*N*-diphenyl-*N'*,*N'*-di-4-*tert*-butylphenyl-1,4-phenylenediamine moieties

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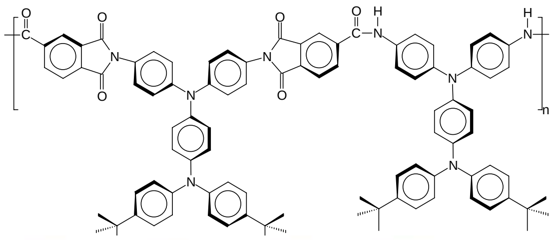
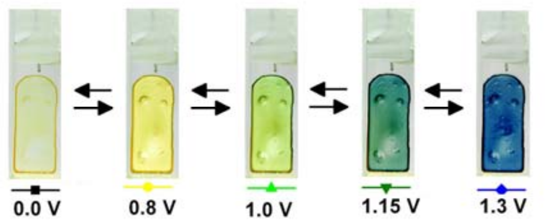
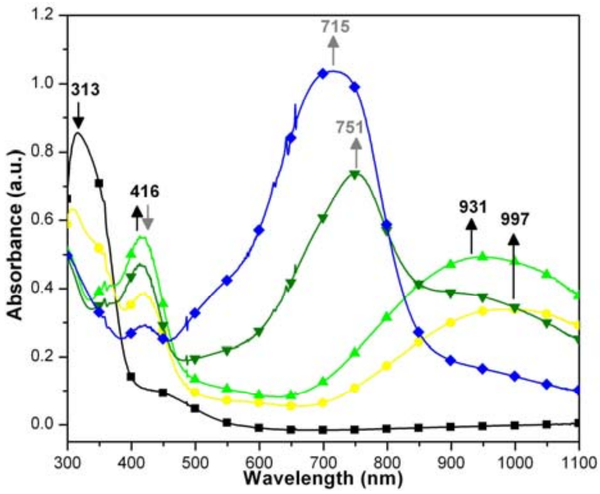
Aromatic polyamides and polyimides containing *N,N,N',N'*-tetraphenyl-1,4-phenylenediamine moieties reveal interesting electrochromic characteristics, such as polyelectrochromism, high coloration efficiency, high optical contrast, and excellent redox stability.[1-4] A new imide ring-preformed dicarboxylic acid monomer, *N*,*N*-bis(4-*tert*-butylphenyl)-*N'*,*N'*-bis(4-trimellitimido)-1,4-phenylenediamine (**2**), was synthesized from the condensation of *N*,*N*-bis(4-aminophenyl)-*N'*,*N'*-bis(4-*tert*-butylphenyl)-1,4-phenylenediamine (**1**) and trimellitic anhydride. A series of new poly(amide-imide)s were prepared from the diimide-diacid **2** with various aromatic diamines by the phosphorylation polyamidation reaction. All the polymers were readily soluble in many organic solvents and could be solution-cast into tough and flexible polymer films with moderate to high glass-transition temperatures of 280–320 ^{o}C. Cyclic voltammograms of the poly(amide-imide) films cast onto the indium-tin oxide (ITO)-coated glass substrate exhibited two to four reversible oxidation redox couples at 0.68–0.69 V and 1.06–1.10 V *vs.* Ag/AgCl in acetonitrile solution, and they revealed high redox and electrochromic stability. The poly(amide-imide) with the following structure displayed several coloration changes upon oxidation at varying applied voltages.







[1] Cheng, S.-H.; Hsiao, S.-H.; Su, T.-H.; Liou, G.-S. *Macromolecules* **2005**, *38*, 307.
[2] Liou, G.-S.; Chang, C.-W. *Macromolecules* **2008**, *41*, 1667.
[3] Chang, C.-W.; Chung, C.-H.; Liou, G.-S. *Macromolecules* **2008**, *41*, 8441.
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Abstract

Aromatic polyamides and polyimides containing *N,N,N',N'*-tetraphenyl-1,4-phenylenediamine moieties reveal interesting electrochromic characteristics, such as polyelectrochromism, high coloration efficiency, high optical contrast, and excellent redox stability.[1-4] A new imide ring-preformed dicarboxylic acid monomer, *N,N*-bis(4-*tert*-butylphenyl)-*N',N'*-bis(4-trimellitimido)-1,4-phenylenediamine (**2**), was synthesized from the condensation of *N,N*-bis(4-aminophenyl)-*N',N'*-bis(4-*tert*-butylphenyl)-1,4-phenylenediamine (**1**) and trimellitic anhydride. A series of new poly(amide-imide)s were prepared from the diimide-diacid **2** with various aromatic diamines by the phosphorylation polyamidation reaction. All the polymers were readily soluble in many organic solvents and could be solution-cast into tough and flexible polymer films with moderate to high glass-transition temperatures of 280–320 °C. Cyclic voltammograms of the poly(amide-imide) films cast onto the indium-tin oxidem (ITO)-coated glass substrate exhibited two to four reversible oxidation redox couples at 0.68–0.69 V and 1.06–1.10 V *vs.* Ag/AgCl in acetonitrile solution, and they revealed high redox and electrochromic stability. The poly(amide-imide) with TPPA structure displayed several coloration changes upon oxidation at varying applied voltages.

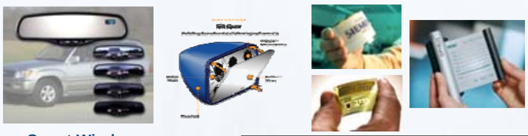
Introduction

What is electrochromism ?

Electrochromism refers to the reversible color change of electrochromic materials, during the electrochemical redox reaction.[5-8]

Electrochromic Technology

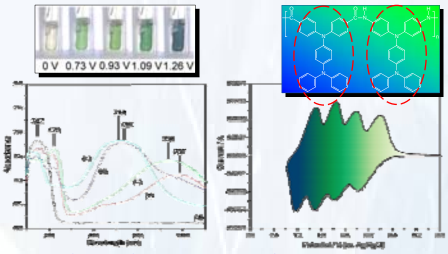
- Car Anti-Glazing Rear-View Mirrors
- Electrochromic Displays



- Smart Windows

Literature Discussion

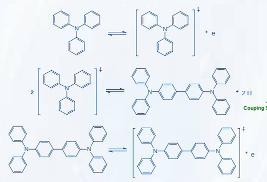
Multiple Electrochromism of Aromatic Polyamides



Liou G.-S.; Hsiao S.-H.; Su T.-Y. *J. Mater. Chem.*, **2005**, *15*, 1812.

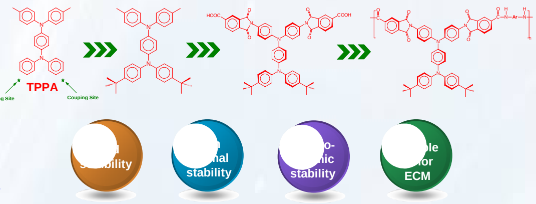
Motivation and Goal

Mechanism of tail-to-tail coupling reaction of triphenylamine



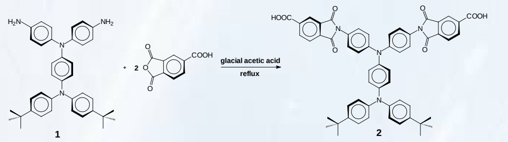
S.-H. Cheng et. al. J Electroana Chem, **2005**, *575*, 95.

Multicolor Electrochromic Poly(amide-imide)s

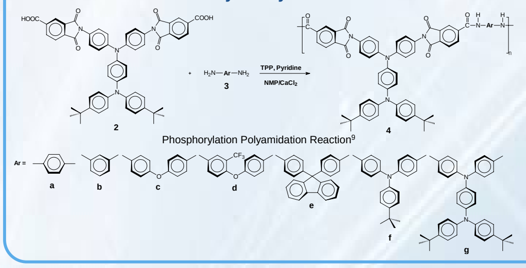


Experimental

Monomer Synthesis

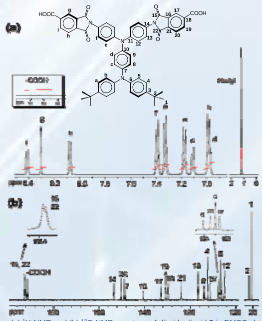


Polymer Synthesis



Structural Characterization

Diimide-dicarboxylic Acid 2 (**brown powder**)
yield: 80 %. mp: 321-323 °C (DSC, 10 °C/min).
IR (KBr): 2700-3400 (O-H stretching), 2964 (*t*-butyl C-H stretch), 1778, 1724 cm^{-1} (imide C═O stretching).



(a) ^{1}H-NMR and (b) ^{13}C-NMR spectrum of diimide-diacid **2** in DMSO-d_6.

Results and Discussion

Thermal properties of PAI[a]

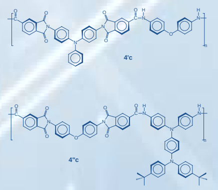
Polymer code	T_g[b] (°C)	T_s[c] (°C)	T_d[d] at 5 wt % loss (°C) In N_2	T_d[d] at 5 wt % loss (°C) In air	T_d[d] at 10 wt % loss (°C) In N_2	T_d[d] at 10 wt % loss (°C) In air	Char yield[e] (wt %)
4a	314	290	423	434	470	493	64
4b	299	272	453	455	512	515	65
4c	280	260	447	451	495	515	66
4d	284	250	449	451	523	498	64
4e	320	289	486	481	535	540	68
4f	293	278	477	463	533	521	69
4g	282	255	477	516	532	553	70

[a] Midpoint temperature of the baseline shift on the second DSC heating trace (rate= 20 °C/min) of the sample after quenching from 400 to 50 °C (rate= 200 °C/min) in nitrogen.
[b] Softening temperature measured by TMA with a constant applied load of 10 mN at a heating rate of 10 °C/min.
[c] Decomposition temperature at which a 5% or 10% weight loss was recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 20 cm^3/min.
[d] Residual weight percentage at 800 °C in nitrogen.

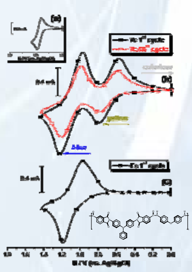
Optical and electrochemical properties of PAIs

Polymer code	In solution: abs λ_{max} (nm)[a]	In solution: PL λ_{max} (nm)[a]	In solution: Φ_F[b] (%)	As film: abs λ_{max} (nm)	As film: abs λ_{onset} (nm)	Oxidation potential[c] (V) (vs. Ag/AgCl in CH_3CN) First E_{onset}	First $E_{1/2}$	Second $E_{1/2}$	Third $E_{1/2}$	Fourth $E_{1/2}$	E_g[d] (eV)	HOMO[e] (eV) E_{onset}	HOMO[e] (eV) $E_{1/2}$	LUMO[e] (eV) E_{onset}	LUMO[e] (eV) $E_{1/2}$
4a	312	369	0.53	306	417	0.44	0.68	1.07	–	–	2.97	4.80	5.04	1.83	2.07
4b	313	373	0.47	307	405	0.46	0.69	1.06	–	–	3.06	4.82	5.05	1.76	1.99
4c	306	376	0.45	306	401	0.42	0.69	1.04	–	–	3.09	4.78	5.05	1.69	1.96
4d	311	385	0.23	307	401	0.47	0.68	1.07	–	–	3.09	4.83	5.04	1.74	1.95
4e	311	371	0.47	311	400	0.45	0.69	1.10	–	–	3.10	4.81	5.05	1.71	1.95
4f	310	370	0.37	317	428	0.47	0.69	0.89	1.05	–	2.89	4.83	5.05	1.94	2.16
4g	313	376	0.26	316	460	0.42	0.63	0.69	0.95	1.04	2.70	4.78	4.99	2.08	2.29
4'c	304	368	0.22	301	400	0.82	1.00	–	–	–	3.10	5.18	5.36	2.08	2.26
4''c	310	435	0.97	308	424	0.43	0.56	0.95	–	–	2.92	4.79	4.92	1.87	2.00

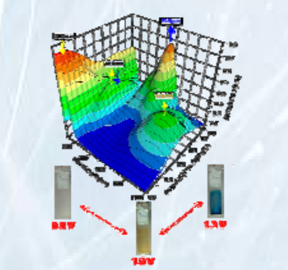
[a] Measured in dilute solution in NMP at a concentration of about 10^{-5} mol/L. [b] The quantum yield in dilute solution was calculated in an integrating sphere with quinine sulfate as the standard (Φ_F = 54.6%). [c] Oxidation potentials from cyclic votammograms. [d] Energy gap = 1240/ Abs λonset of the polymer film. [e] The HOMO energy levels were calculated from $E_{1/2}$ and were referenced to ferrocene (4.8 eV). [f] LUMO = HOMO - E_g.



CV of PAIs 4c & 4'c

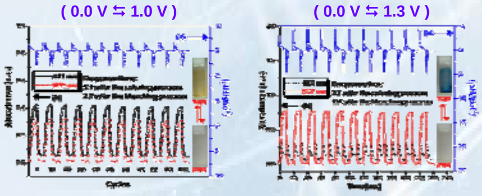


3-D Spectroelectrochemical Behavior

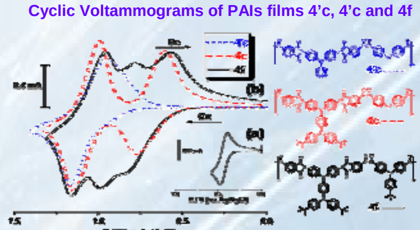


Electrochromic Switching of PAI 4c

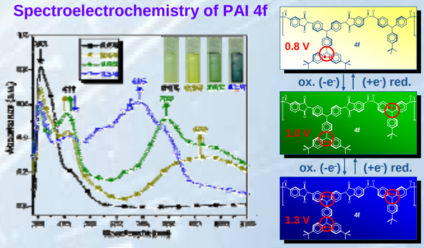
(0.0 V ⇆ 1.0 V) (0.0 V ⇆ 1.3 V)



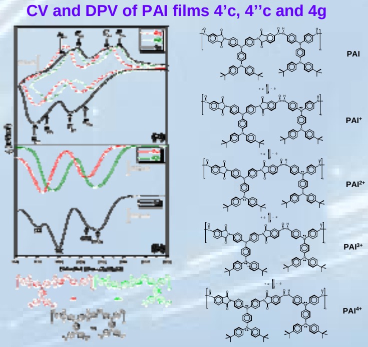
Cyclic Voltammograms of PAIs films 4'c, 4'c and 4f



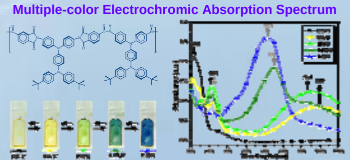
Spectroelectrochemistry of PAI 4f



CV and DPV of PAI films 4'c, 4''c and 4g



Multiple-color Electrochromic Absorption Spectrum



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