

# Synthesis, Photoluminescence, and Electrochromism of Novel Polyamides with 3,6-Di-*tert*-butylcarbazol-9-yl-substituted Triphenylamine Units

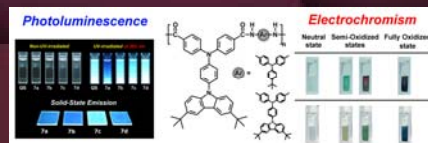
Hui-Min Wang, Sheng-Huei Hsiao\*

Department of Chemical Engineering and Biotechnology, National Taipei University of Technology,  
1 Chunghsiao East Road, Section 3, Taipei 10608, Taiwan  
E-mail: shhsiao@ntut.edu.tw



## ABSTRACT

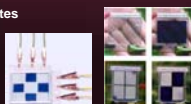
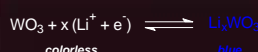
A series of six novel aromatic polyamides 7a-7f with main-chain triphenylamine and pendent 3,6-bis(*tert*-butyl)carbazole units were prepared from a newly synthesized dicarboxylic acid monomer, 4,4'-dicarboxy-4''-(3,6-di-*tert*-butylcarbazol-9-yl)triphenylamine, and various aromatic diamines. These polyamides were amorphous with good solubility in many organic solvents and could be solution-cast into flexible and strong films. In addition to high  $T_g$  values and good thermal stability, the polyamides also revealed strong blue photoluminescence and good redox stability along with multi-electrochromic behavior.



## INTRODUCTION

### What is Electrochromism ?

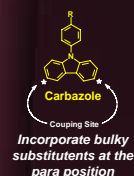
Where the switching of redox states generates new or different visible region bands, the material is said to be electrochromic.<sup>1</sup>



### Electrochromic Technology

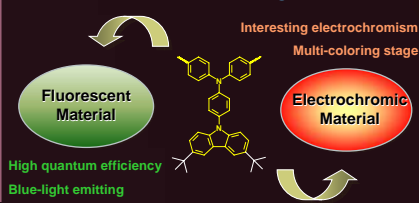


### Motivation



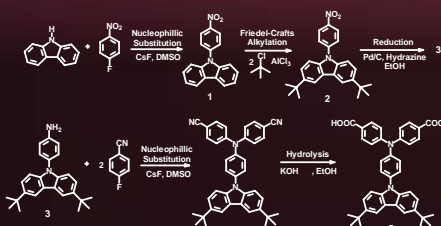
J. Ambrose, et al. J. Electrochem. Soc. 1975, 122, 876.

### Molecular Design

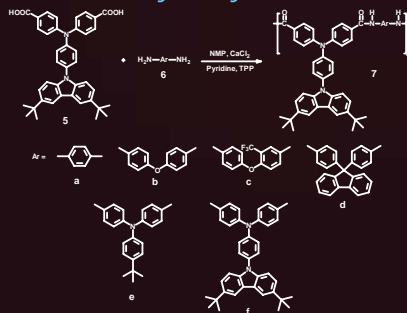


## EXPERIMENTAL

### Monomer Synthesis



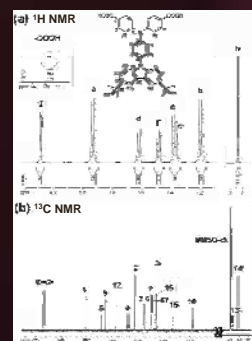
### Polymer Synthesis



### Structural Characterization

Dicarboxylic acid monomer 5 (yellowish crystals)  
Yield: 86%. Mp: 364-366 °C (DSC, 10 °C/min)

### <sup>1</sup>H and <sup>13</sup>C NMR spectra of dicarboxylic acid monomer 5



### The as-prepared sample of polyamide 7d



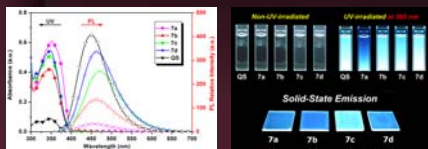
## RESULTS AND DISCUSSION

### Optical Properties

Polymer code	In solution <sup>a</sup>			As film		
	$\lambda_{max}^{abs}$ (nm)	$\lambda_{max}^{PL}$ (nm)	$\Phi_f^b$ (%)	$\lambda_{max}^{abs}$ (nm)	$\lambda_{max}^{abs}$ (nm)	$\lambda_{max}^{PL}$ (nm)
7a	298, 352	457	2.9	298, 350	406	466
7b	298, 351	462	17.0	299, 347	401	457
7c	298, 348	466	21.3	298, 346	400	459
7d	298, 348	465	32.8	300, 347	394	461
7e	298, 351	505	0.4	298, 350	426	—
7f	298, 351	493	0.5	299, 349	421	—

<sup>a</sup> Measured in dilute solutions in NMP at a concentration of about  $1 \times 10^{-4}$  mol/L. <sup>b</sup> Fluorescence quantum yield calculated in an integrating sphere with quinine sulfate as the standard ( $\Phi_f = 54.6\%$ ).

### UV Absorption and Fluorescence

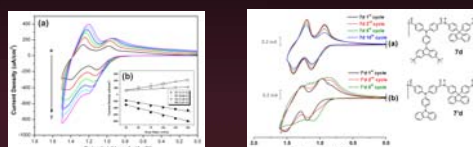


### Electrochromic Properties

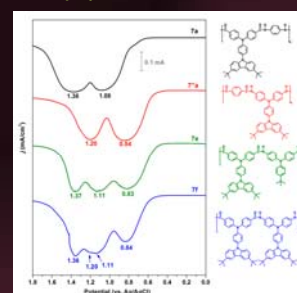
Polymer code	Oxidation potential <sup>a</sup> (V)					$E_g^b$ (eV)		HOMO <sup>c</sup> (eV)		LUMO <sup>d</sup> (eV)	
	$E_{onset}$	$E_{1/2}^{OX1}$	$E_{1/2}^{OX2}$	$E_{1/2}^{OX3}$	$E_{1/2}^{OX4}$	$E_{onset}$	$E_{1/2}$	$E_{onset}$	$E_{1/2}$	$E_{onset}$	$E_{1/2}$
7a	0.91	1.10	1.41	—	—	3.05	5.27	5.47	2.22	2.42	—
7a	0.97	1.06	1.52 <sup>e</sup>	—	—	3.07	5.33	5.42	2.26	2.35	—
7b	0.97	1.09	1.34	—	—	3.09	5.33	5.45	2.24	2.36	—
7c	0.92	1.04	1.32	—	—	3.10	5.28	5.40	2.18	2.30	—
7d	0.91	1.03	1.30	—	—	3.15	5.27	5.39	2.12	2.24	—
7'd	0.97	1.09	1.40 <sup>e</sup>	—	—	3.12	5.33	5.44	2.21	2.32	—
7e	0.66	0.79	1.10	1.34	—	2.91	5.06	5.17	2.15	2.26	—
7f	0.65	0.71	1.14	1.25	1.38	2.95	5.07	5.20	2.12	2.25	—
7'a	0.68	0.83	1.18	—	—	3.07	5.04	5.19	1.97	2.12	—

<sup>a</sup> Oxidation potentials from cyclic voltammograms (vs. Ag/AgCl in CH<sub>2</sub>Cl<sub>2</sub>). <sup>b</sup> Energy gap =  $1240/\lambda_{max}$  of the polymer film. <sup>c</sup> The HOMO energy levels were calculated from  $E_{1/2}^{OX1}$  or  $E_{1/2}^{OX2}$ , referred to ferrocene (4.8 eV). <sup>d</sup> LUMO = HOMO -  $E_g$ . <sup>e</sup> Irreversible peak potential ( $E_p$ ).

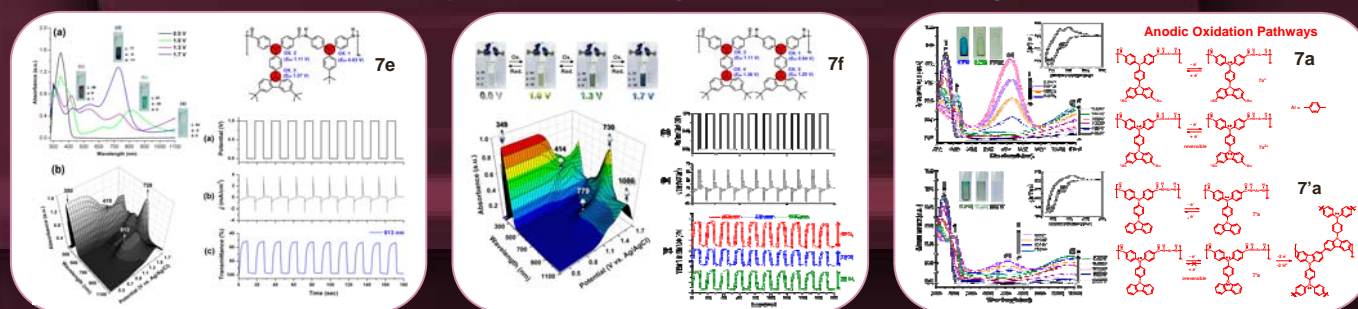
### Cyclic Voltammograms of Polyamide 7d and 7'd



### Differential Pulse Voltammograms of polyamides 7a, 7'a, 7e and 7f



### Spectroelectrochemistry and Electrochromic Switching



## REFERENCES

- P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, *Electrochromism and Electrochromic Devices*, Cambridge University Press, Cambridge, UK, 2007.
- P. M. Beaujuge and J. R. Reynolds, *Chem. Rev.*, 2010, 110, 268.
- D. R. Rosseinsky and R. J. Mortimer, *Adv. Mater.*, 2001, 13, 783.
- G. Sonmez and H. B. Sonmez, *J. Mater. Chem.*, 2006, 16, 2473.
- R. Baetens, B. P. Jelle and A. Gustavsen, *Sol. Energy Mater. Sol. Cells*, 2010, 94, 87.
- S. Beaupre, A.-C. Breton, J. Dumas and M. Leclerc, *Chem. Mater.*, 2009, 21, 1504.
- M. Thelakkat, *Macromol. Mater. Eng.*, 2002, 287, 442.
- Y. Shirota and H. Kageyama, *Chem. Rev.*, 2007, 107, 953.