Star-like polyaniline : synthesis, layer-by-layer assembly and electrochromism

Jia, Pengtao

2011

Jia, P. (2011). Star-like polyaniline : synthesis, layer-by-layer assembly and electrochromism. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/42904>

<https://doi.org/10.32657/10356/42904>

**STAR-LIKE POLYANILINE: SYNTHESIS, LAYER-BY-
LAYER ASSEMBLY AND ELECTROCHROMISM**

JIA PENGTAO

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2011

**STAR-LIKE POLYANILINE: SYNTHESIS, LAYER-BY-
LAYER ASSEMBLY AND ELECTROCHROMISM**

JIA PENGTAO

School of Materials Science and Engineering

A thesis submitted to the Nanyang Technological University in fulfillment of
the requirement of the degree of Doctor of Philosophy

2011

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my sincere thanks to all those who offered her/his guidance, help and support during my PhD study.

First of all, I would like to express my deepest appreciation to my supervisor and mentor, Associate Professor Lu Xuehong, Division of Materials Technology, School of Materials Science and Engineering (MSE), for her invaluable guidance, support, encouragement throughout this work and her patience in revising my papers and reports. I am very fortunate to have the opportunity to study and work with her.

I would like to extend my heartfelt thanks to my co-supervisor, Dr. Xu Jianwei, Institute of Materials Research and Engineering (IMRE), for his indispensable advice, valuable help and guidance.

I would like to express my gratitude to my Master's advisor Prof. Ge Lingmei, Xi'an University of Science and Technology, for her encouragement, support, care and help all the time.

I would like to give my thanks to Prof. Paula T. Hammond and Dr. Avni A. Argun, Department of Chemical Engineering, Massachusetts Institute of Technology, for their support, valuable help and indispensable advice.

I will also like to thank the technical staffs from Organic Materials Cluster, Inorganic Materials Cluster and Service Cluster in MSE, and Dr. Zhang Zheng, Mr. Li Teng Hui, Ms. Hui Hui Kim from IMRE for sharing their technical know-how on the operation of

various characterization equipments and going the extra mile to help me solve any technical problems I had.

I would like to acknowledge my fellow colleagues, namely Dr. Xiong Shanxin, Dr. Ng Kok Peng Joseph, Mr. Yee Wu Aik for their assistance and valuable input.

I would like to thank my parents, my elder brother and my wife for all their love, understanding, care and encouragement.

I am also grateful to Nanyang Technological University and Temasek Laboratories for their financial support. Last but not least, my sincere gratitude to all the colleagues and friends who have in one way or another, make a difference during my project work in MSE.

LIST OF ABBREVIATIONS

PANI	Polyaniline
EB	Emeraldine base
ES	Emeraldine salt
SPANI	Self-doped polyaniline
OAPS	Octa(aminophenyl) silsesquioxane
POSS	Polyhedral oligomeric silsesquioxane
POSS-PANI	Polyhedral oligomeric silsesquioxane-polyaniline
CP	Cyclotriphosphazene
HNCP	Hexa(4-nitrophenoxy) cyclotriphosphazene
HACP	Hexa(4-aminophenoxy) cyclotriphosphazene
HACP-PANI	Hexa(4-aminophenoxy) cyclotriphosphazene-polyaniline
PDMA	Poly(2,5-dimethoxy aniline)
PEDOT	Poly(3,4-ethylenedioxythiophene)
PProDOT	Poly(3,4-propylenedioxythiophene)
DBSA	Dodecylbenzenesulfonic acid
PAMPS	Poly(2-acrylamido-methane-2-propanesulfonic acid)
PSS	Poly(styrene sulfonate)
LPEI	Linear poly(ethylene imine)
PB	Prussian blue
PXV	Poly(hexyl viologen)
P(3HT-co-3TPP)	Poly[3-hexylthiophene-co-N-(3-trimethoxysilylpropyl) pyrrole]
PTOESA	Poly(2-(3thienyloxy)ethanesulfonic acid)

DDS	4,4'-diaminodiphenyl sulfide
[BMIM][PF ₆]	1-butyl-3-methylimidazolium hexafluorophosphate
[BMIM][BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborate
[BMIM][Br]	1-butyl-3-methylimidazolium bromide
[BMIM][Tf ₂ N]	1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonimide
[BMPY][Tf ₂ N]	1-butyl-1-methylpyrrolidinium bis(trifluoromethane)sulfonimide
APS	Ammonium peroxydisulfate
PC	Propylene carbonate
EC	Ethylene carbonate
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PVA	Poly(vinyl alcohol)
PMMA	Poly(methyl methacrylate)
PVDF-HFP	Poly(vinylidene fluoride)-hexafluoropropylene
DMSO	Dimethyl sulfoxide
DMAc	N,N-Dimethylacetamide
ITO	Indium tin oxide
PET	Poly(ethylene terephthalate)
Fc	Ferrocene
WE	Working electrode
CE	Counter electrode
RE	Reference electrode
FWHM	Full-width at half-maximum
BE	Binding energy
LbL	Layer-by-layer
IR	Infrared

NIR	Near-infrared
FTIR	Fourier transform infrared
EIMS	Electron-impact mass spectrometry
SEC	Size exclusion chromatography
WAXD	Wide angle X-ray diffraction
TLC	Thin layer chromatographic analysis
NMR	Nuclear magnetic resonance
FESEM	Field-emission scanning electron microscope
TEM	Transmission electron microscopy
AFM	Atomic force microscope
XPS	X-ray photoelectron spectroscopy
CV	Cyclic voltammetry
UV-Vis-NIR	Ultra violet-visible-near infrared

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	I
LIST OF ABBREVIATIONS	III
TABLE OF CONTENTS.....	VI
LIST OF FIGURES, SCHEMES & TABLES.....	IX
ABSTRACT.....	XIV
1. INTRODUCTION.....	1
1.1 Background	1
1.2 Star-like conjugated polymers.....	2
1.3 Layer-by-layer (LbL) assembly of polymeric multilayer thin films	3
1.4 Motivation and objectives	3
1.5 Organization of the thesis.....	5
2. LITERATURE REVIEW	7
2.1 Electrochromic materials	7
2.1.1 Electrochromism	7
2.1.2 Types of electrochromic materials.....	7
2.1.2.1 Inorganic electrochromic materials	7
2.1.2.2 Organic electrochromic materials	8
2.1.2.3 Hybrid materials.....	10
2.1.2.4 Nanocomposites	11
2.1.2.5 Comparison between inorganic electrochromic materials and electrochromic polymers	12
2.1.3 Typical electrochromic conjugated polymers.....	13
2.1.3.1 PANI.....	13
2.1.3.2 PEDOT	15
2.1.4 Doping	16
2.2 Electrochromic devices and applications	17
2.2.1 Transmission electrochromic devices	17
2.2.2 Reflective electrochromic device.....	20
2.2.3 Fabrication techniques for electrochromic devices.....	21
2.2.4 Applications of electrochromic devices	23
2.3 Electrochromic performance parameters	25
2.3.1 Electrochromic contrast.....	25
2.3.2 Switching speed	25
2.3.3 Coloration efficiency.....	26
2.3.4 Cycle Life	26
2.4 Characterization of electrochemical and electrochromic properties	27
2.4.1 Electrochemical cell with three electrodes	27

2.4.2 Characterization methods	28
2.4.2.1 Cyclic voltammetry	28
2.4.2.2 Chronoamperometry.....	28
2.4.2.3 Spectroelectrochemistry	28
2.4.2.4 Electrochromic switching study.....	29
3. SYNTHESIS, CHARACTERIZATION AND ELECTROCHROMIC PROPERTIES OF DBSA-DOPED HACP-PANI COPOLYMERS	30
3.1 Introduction	30
3.2 Experimental sections	31
3.2.1 Materials	31
3.2.2 Structural analysis	31
3.2.3 Monomer synthesis	32
3.2.4 Polymerization	32
3.2.5 Device fabrication and characterization	33
3.2.6 Molecular simulation.....	34
3.3 Results and discussion	35
3.3.1 Chemical structure of the copolymers.....	35
3.3.2 Spectroelectrochemical characterization.....	37
3.3.3 Electrochromic switching studies	39
3.3.4 Crystallization of the copolymers	40
3.4 Conclusions	44
4. SYNTHESIS, LBL ASSEMBLY AND ELECTROCHROMIC PROPERTIES OF HACP-PANI/PAMPS MULTILAYER THIN FILMS	45
4.1 Introduction	45
4.2 Experimental section.....	46
4.2.1 Materials	46
4.2.2 Preparation of HACP-PANI-EB	46
4.2.3 Structural analysis	47
4.2.4 Preparation of dipping solutions	47
4.2.5 LbL assembly of multilayer thin films	47
4.2.6 Thin film characterization	48
4.3 Results and discussion	48
4.3.1 Synthesis and structural verification	48
4.3.2 LbL assembly of multilayer thin films	51
4.3.3 CV studies.....	54
4.3.4 Spectroelectrochemical characterization.....	55
4.3.5 Electrochromic switching studies	56
4.3.6 Surface morphology	57
4.4 Conclusions	59
5. SYNTHESIS, LBL ASSEMBLY AND ELECTROCHROMIC PROPERTIES OF POSS-BASED STAR-LIKE POLYANILINE	60
5.1 Introduction	60
5.2 Experimental Section	61
5.2.1 Materials	61
5.2.2 Preparation of POSS-PANI-EB	61
5.2.3 Structural analysis	62

5.2.4 Preparation of dipping solutions and LbL assembly of multilayer thin films ..	62
5.2.5 Thin film characterization	62
5.3 Results and discussion	63
5.3.1 Synthesis and structural verification	63
5.3.2 LbL assembly of multilayer thin film	66
5.3.3 Surface morphology	68
5.3.4 CV studies.....	69
5.3.5 Spectroelectrochemical characterization.....	74
5.3.6 Electrochromic switching studies	75
5.4 Conclusions	78
 6. HIGH-CONTRAST ELECTROCHROMIC THIN FILMS VIA LBL ASSEMBLY OF STAR-LIKE AND SULFONATED POLYANILINE	 80
6.1 Introduction	80
6.2 Experimental Section	81
6.2.1 Materials	81
6.2.2 Preparation of dipping solutions	82
6.2.3 LbL assembly of multilayer thin films	82
6.2.4 Thin film characterization	82
6.3 Results and discussion	84
6.3.1 Interactions between POSS-PANI and SPANI.....	84
6.3.2 CV studies.....	91
6.3.3 Spectroelectrochemical characterization.....	92
6.3.4 Electrochromic switching studies	94
6.3.5 Complementary electrochromic device.....	97
6.3.5.1 Electrochromic property of PEDOT:PSS	97
6.3.5.2 Electrochromic properties of the device	98
6.4 Conclusions	101
 7. CONCLUSIONS AND RECOMMENDATIONS.....	 102
7.1 Conclusions	102
7.2 Recommendations for future research	103
 REFERENCES.....	 106
 LIST OF PUBLICATIONS	 116

LIST OF FIGURES, SCHEMES & TABLES

Figure	Page
Figure 1.1 Structures of (a) POSS and (b) CP.	3
Figure 1.2 The scope of my Ph.D work.....	5
Figure 2.1 The repeat units of the common conjugated polymers.....	8
Figure 2.2 The structures of PEDOT and its derivatives.....	9
Figure 2.3 The structures of DDP-A and DDB-P.	10
Figure 2.4 The structures of PTOESA and PBETH.....	12
Figure 2.5 Four types of PANI from the fully reduced (leucoemeraldine) to the fully oxidized (pernigraniline) forms.....	14
Figure 2.6 Electrochromic switching for PEDOT:PSS.	16
Figure 2.7 (a) A single-layer electrochromic device with a sandwich structure and (b) complementary electrochromic device.....	19
Figure 2.8 Reflective electrochromic device configuration.....	21
Figure 2.9 Diagram of LbL assembly.....	22
Figure 2.10 Electrochromic applications of (a) e-paper, (b) smart sunglasses and (c) smart windows.	24
Figure 2.11 The configuration of three-electrode electrochemical cell in a cuvette.....	27
Figure 3.1 ³¹ P NMR spectra of (a) HACP and (b) 4.0%HACP-PANI copolymer.	36
Figure 3.2 Visible spectra of the electrochromic devices with (a) PANI, (b) 0.5%HACP-PANI, (c) 2.0%HACP-PANI, (d) 4.0%HACP-PANI and (e) HACP/PANI blend (4.0 mol. % HACP) as the electrochromic layers, respectively, at different potentials (–2.0, –1.0, 0.0, +1.0, +2.0 V).....	38
Figure 3.3 Optical switching for the devices with 4.0%HACP-PANI and PANI as electrochromic layers separately, under square-wave potentials oscillating between –2.0 and +2.0 V.....	39
Figure 3.4 Conformation of HACP with minimized potential obtained from molecular dynamics simulation.	40
Figure 3.5 (a) X-ray diffraction patterns and (b) crystal thickness estimated from FWHM of the copolymers.	41

Figure 3.6 FESEM images of (a) PANI, (b) 0.5%HACP-PANI, (c) 2.0%HACP-PANI and (d) 4.0%HACP-PANI.....	42
Figure 3.7 A TEM image of 4.0%HACP-PANI	42
Figure 3.8 Ionic and electrical conductivity of PANI and HACP-PANI copolymers.	43
Figure 4.1 The possible configurations of (a) HACP-PANI/DBSA and (b) POSS-PANI/DBSA.....	45
Figure 4.2 FTIR spectra of (a) HACP, (b) PANI-EB and (c) 4%HACP-PANI-EB.	50
Figure 4.3 XPS P 2p of (a) HACP and (b) 4%HACP-PANI-EB.....	51
Figure 4.4 Plots of absorbance of the PANI/PAMPS and 4%HACP-PANI/PAMPS multilayer films (5 bilayers) adsorbed on glass substrates as a function of dipping time.	52
Figure 4.5 (a) Growth curves for LbL assembled PANI/PAMPS and 4%HACP-PANI/PAMPS thin films on glass and (b) a photograph of (4%HACP-PANI/PAMPS) ₄₅	53
Figure 4.6 (a) P 2p XPS spectrum of (4%HACP-PANI/PAMPS) _{15.5} on silicon wafer and (b) comparison of the P 2p XPS spectra of 4%HACP-PANI-EB and (4%HACP-PANI/PAMPS) _{15.5} thin films on silicon wafer.	53
Figure 4.7 CV curves of (a) (PANI/PAMPS) ₄₅ and (b) (4.0%HACP-PANI/PAMPS) ₄₅ measured in a 0.1 M LiClO ₄ /acetonitrile solution with scan rate of 10, 25, 50, 75 and 100 mV/s, respectively, using silver wire as the reference electrode.....	55
Figure 4.8 Visible spectra of (a) (PANI/PAMPS) ₄₅ and (b) (4%HACP-PANI/PAMPS) ₄₅ under different potentials (−0.3, 0, +0.2, +0.3, +0.5, +0.7, +0.9 V). (c) UV-Vis-NIR spectra of (PANI/PAMPS) ₄₅ and (4%HACP-PANI/PAMPS) ₄₅	56
Figure 4.9 Optical switching for (PANI/PAMPS) ₄₅ and (4%HACP-PANI/PAMPS) ₄₅ with 100 nm thickness.	57
Figure 4.10 FESEM images of (a) (PANI/PAMPS) _{15.5} with PANI on top and (b) (4%HACP-PANI/PAMPS) _{15.5} with 4%HACP-PANI on top.....	58
Figure 5.1 FTIR spectra of (a) OAPS, (b) PANI-EB, (c) 1%POSS-PANI-EB and (d) 4%POSS-PANI-EB	65
Figure 5.2 Plots of absorbance of PANI/PAMPS and 1%POSS-PANI/PAMPS multilayer films (5 bilayers) adsorbed on glass substrates as a function of dipping time.....	66
Figure 5.3 Growth curves for LbL assembled PANI/PAMPS and 1%POSS-PANI/PAMPS thin films on glass.....	67
Figure 5.4 Si 2p XPS spectra of (a) (1%POSS-PANI/PAMPS) ₁₅ on silicon wafer and (b) silicon wafer.	68
Figure 5.5 Tapping mode AFM images of (a) (PANI/PAMPS) _{15.5} with PANI on top and (b) (1%POSS-PANI/PAMPS) _{15.5} with 1%POSS-PANI on top.....	69

Figure 5.6 FESEM images of (a) (PANI/PAMPS) _{15.5} with PANI on top and (b) (1%POSS-PANI/PAMPS) _{15.5} with 1%POSS-PANI on top.....	69
Figure 5.7 CV curves of (a) (PANI/PAMPS) ₅₀ and (b) (1.0%POSS-PANI/PAMPS) ₅₀ measured in a 0.1M LiClO ₄ /acetonitrile solution with scan rate of 10, 25, 50, 75 and 100 mV/s, respectively, using silver wire as the reference electrode. (c) plots of peak current densities vs. scan rate. (d) plots of peak current densities vs. square root of scan rate.	71
Figure 5.8 CV curves of a spin-coated 1%POSS-PANI/PSS film with 100 nm thickness measured in a 0.1M LiClO ₄ /acetonitrile solution with scan rate of 10, 25, 50, 75 and 100 mV/s, respectively, using silver wire as the reference electrode.....	73
Figure 5.9 The anodic-cathodic peak separation of (PANI/PAMPS) ₅₀ and (1%POSS-PANI/PAMPS) ₅₀	74
Figure 5.10 Visible spectra of (a) (PANI/PAMPS) ₅₀ and (b) (1%POSS-PANI/PAMPS) ₅₀ under different potentials (−0.4, −0.1, +0.1, +0.2, +0.4, +0.6, +0.8, +1.0 V). (c) UV-Vis-NIR spectra of (PANI/PAMPS) ₅₀ and (1%POSS-PANI/PAMPS) ₅₀ . (d) A photograph of (1%POSS-PANI/PAMPS) ₅₀	75
Figure 5.11 Optical switching of (PANI/PAMPS) ₅₀ and (1%POSS-PANI/PAMPS) ₅₀ with 100 nm thickness.	77
Figure 5.12 Optical switching of 1%POSS-PANI/PSS film with 100 nm thickness.....	77
Figure 5.13 Optical switching of (1%POSS-PANI/PAMPS) ₅₀ and (1%POSS-PANI/PAMPS) ₉₉	78
Figure 6.1 Configuration of the complementary electrochromic device of ITO-glass (POSS-PANI/SPANI) ₅₀ [BMIM]PF ₆ -PVDF(HFP) PEDOT:PSS ITO-glass.....	83
Figure 6.2 (a) A scheme showing the structure of POSS-PANI/SPANI multilayer films, (b) the growth curve for LbL assembly of POSS-PANI/SPANI multilayer films on glass....	84
Figure 6.3 XPS N 1s of (a) spin-coated SPANI, (b) (POSS-PANI/SPANI) ₁₅ and (c) (POSS-PANI/SPANI) _{15.5}	85
Figure 6.4 Plots of the corrected N 1s and S 2p core-level spectra for (a) (POSS-PANI/SPANI) ₁₅ and (b) (POSS-PANI/SPANI) _{15.5}	87
Figure 6.5 (a) UV-Vis-NIR spectra of the spin-coated SPANI, (POSS-PANI/PAMPS) ₅₀ and (POSS-PANI/SPANI) ₅₀ , (b) polaron absorption of the spin-coated SPANI, (POSS-PANI/PAMPS) ₅₀ and (POSS-PANI/SPANI) ₅₀ , and (c) plot of $(\alpha h\nu)^2$ vs. $h\nu$ for spin-coated SPANI, (POSS-PANI/PAMPS) ₅₀ and (POSS-PANI/SPANI) ₅₀	89
Figure 6.6 X-ray diffraction patterns of spin-coated SPANI, (POSS-PANI/PAMPS) ₅₀ and (POSS-PANI/SPANI) ₅₀	90
Figure 6.7 CV curves of (a) (POSS-PANI/SPANI) ₅₀ and (b) spin-coated SPANI measured in a 0.1M LiClO ₄ /acetonitrile solution with scan rate of 10, 25, 50, 75 and 100 mV/s, respectively, using silver wire as the reference electrode. (c) CV curves of (POSS-PANI/PAMPS) ₅₀ (blue line), spin-coated SPANI (black line) and (POSS-PANI/SPANI) ₅₀ (red line) measured in a 0.1 M LiClO ₄ /acetonitrile solution with scan rate of 25 mV/s. (d)	

plots of peak current densities vs. scan rate and (e) plots of peak current densities vs. square root of scan rate.	92
--	----

Figure 6.8 Visible spectra of (a) (POSS-PANI/SPANI) ₅₀ , (b) spin-coated SPANI under different potentials (−0.4, −0.1, +0.1, +0.2, +0.4, +0.6, +0.8 V) and (c) the absorbance curves under +0.8 V (solid lines) and −0.4 V (dash lines) for (POSS-PANI/SPANI) ₅₀ (red line), (POSS-PANI/PAMPS) ₅₀ (blue line) and spin-coated SPANI (black line).	94
---	----

Figure 6.9 Optical switching of (POSS-PANI/SPANI) ₅₀ , (POSS-PANI/PAMPS) ₅₀ and spin-coated SPANI with 100 nm thickness	96
---	----

Figure 6.10 CV curves of (a) PEDOT:PSS with 100 nm thickness measured in a 0.1 M LiClO ₄ /acetonitrile solution with scan rate of 10, 25, 50, 75 and 100 mV/s. (b) Visible spectra of PEDOT:PSS under different potentials (+0.4, +0.2, −0.1, −0.2, −0.3, −0.4, −0.5, −0.6, −0.7 V). (c) Visible spectra of PEDOT:PSS under +0.4 V and −0.7 V and (1%POSS-PANI/SPANI) ₅₀ under −0.4 V and +0.8 V	98
--	----

Figure 6.11 (a) The CV curve of the complementary electrochromic device with scan rate of 25 mV/s. (b) Visible spectra of the device under different potentials (−1.8, −1.5, −1.0, 0, +1.0, +1.5, +1.8 V). (c) Optical switching at 650 nm for the device under square-wave potentials oscillating between −1.7 and +1.7 V.	100
--	-----

Figure 6.12 The photographs of the complementary electrochromic device at (a) transmissive state and (b) absorbing state.....	100
---	-----

Scheme	Page
Scheme 3.1 Synthesis of HACP.....	32
Scheme 3.2 Synthesis of HACP-PANI copolymers.....	33
Scheme 4.1 Oxidative copolymerization of HACP and aniline to form HACP-PANI-ES, followed by conversion to HACP-PANI-EB.....	49
Scheme 4.2 Possible fabrication process for HACP-PANI/PAMPS multilayer thin films	58
Scheme 5.1 Oxidative copolymerization of OAPS and aniline to form POSS-PANI-ES, followed by conversion to POSS-PANI-EB.....	63

Table	Page
Table 2.1 Comparison between inorganic materials and electrochromic polymers.....	13
Table 2.2 Organic electrolytes for use in electrochromic devices.	19
Table 3.1 SEC results of PANI and HACP-PANI copolymers.	37
Table 5.1 Comparison of OAPS and HACP	61
Table 5.2 Elemental analysis data for PANI-EB and 4%POSS-PANI-EB.	65

Table 5.3 Composition of the multilayer films obtained from XPS analysis of (1%POSS-PANI/PAMPS) ₁₅	73
Table 6.1 N 1s data of various samples obtained from XPS analysis.	86
Table 6.2 Band gap and electrical conductivity.	90
Table 6.3 Electrochromic properties of all samples.	96

ABSTRACT

Electrochromism is a phenomenon related to reversible color transformation of a material produced by the application of an external electric field. Electrochromic contrast and switching speed are the key performance indicators for an electrochromic material. The motivation of this work is to make use of cyclotriphosphazene (CP) and polyhedral oligomeric silsesquioxane (POSS) to synthesize novel star-like electrochromic conjugated polymers and study the synergistic effect of star-like structure and film fabrication techniques on electrochromic properties.

Firstly, a new series of electrochromic hexa(4-aminophenoxy) cyclotriphosphazene-polyaniline copolymers (HACP-PANI) were synthesized. Dodecylbenzenesulfonic acid (DBSA) doped 4.0%HACP-PANI (4%HACP-PANI/DBSA) exhibits a significant enhancement in electrochromic contrast as compared with DBSA-doped homopolyaniline (PANI/DBSA). The contrast enhancement can be attributed to the easier diffusion of cations in the film of 4%HACP-PANI/DBSA, as evidenced by a significant increase in ionic conductivity, whereas the switching speed of 4%HACP-PANI/DBSA is not improved significantly due to the excessive external dopants. In order to avoid using excessive amounts of doping acid, HACP-PANI and POSS-PANI copolymers in emeraldine base form were synthesized and fabricated into multilayer thin films with poly(2-acrylamido-methane-2-propanesulfonic acid) (PAMPS) via layer-by-layer (LbL) assembly. However, the contrast and switching kinetics of 4%HACP-PANI/PAMPS is not improved compared with those of PANI/PAMPS under dynamic switching because of its densely packed structure brought by the flexible -O- linkage in HACP-PANI.

In contrast to HACP-PANI, POSS-PANI is more rigid because of the absence of the flexible O groups. The electrochromic contrast of 50 bilayers of POSS-PANI/PAMPS

((POSS-PANI/PAMPS)₅₀) is increased by more than 30% over that of 50 bilayers of PANI/PAMPS ((PANI/PAMPS)₅₀) and the switching kinetics of (POSS-PANI/PAMPS)₅₀ is much faster than those of (PANI/PAMPS)₅₀ and spin-coated POSS-PANI/polymeric acid complexes thin film. In order to improve the electrochromic contrast further, fully conjugated polymeric multilayer thin films of POSS-PANI/self-doped polyaniline (SPANI) were fabricated via LbL assembly. The results show that POSS-PANI/SPANI multilayer thin films have more electroactive units, lower band gap energies and higher electrical conductivity values compared with those of POSS-PANI/PAMPS and spin-coated SPANI films. The electrochromic contrast of 50 bilayers of POSS-PANI/SPANI ((POSS-PANI/SPANI)₅₀) is increased by more than 35% over that of (POSS-PANI/PAMPS)₅₀ and the switching kinetics of (POSS-PANI/SPANI)₅₀ is much faster than that of spin-coated SPANI thin film.

In conclusion, the synergistic combination of the star-like structure of POSS-PANI and LbL assembly is an effective method for PANI to achieve higher contrast and faster switching speed under dynamic switching.

1. INTRODUCTION

1.1 Background

Electrochromism [1-3] refers to the reversible color changes of a material induced by electrochemical processes, such as redox reactions. Electrochromic materials are useful for many applications [4], such as anti-glare car rear-view mirrors, electrochromic strips as battery state-of-charge indicators, smart windows and sunglasses. When electrochromic materials can alter the infrared (IR) emissivity [5], they can also be used for thermal emittance control. There are many types of electrochromic materials, of which conjugated polymers have attracted much attention in recent years due to their high contrast, high coloration efficiency and ease of processing. The most widely used conjugated electrochromic polymer systems are polyaniline (PANI) and its derivatives, and poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives.

Electrochromic contrast and switching speed are the key performance indicators for an electrochromic device. The switching speed is mainly governed by the diffusion of dopants across the electrochromic materials. It has been found that mesoporous electrochromic polymer thin films, which can facilitate dopant ion diffusion [6], and reducing the diffusion distance for the dopant ions through the use of conjugated polymer nanotubes [7] or porous microspheres [8] can greatly improve the switching speed of the devices. However, these methods have insignificant impact on the contrast. A common strategy for improving the contrast of the thiophene-based electrochromic polymers is to manipulate chemical structures of the electrochromic polymers to enlarge the inter-chain distance [9, 10], which could create more accessible doping sites and hence increase the

contrast. Based on the same principle, recently, significant contrast enhancement has also been achieved by tethering conjugated polymer chains onto polyhedral oligomeric silsesquioxane (POSS) nanocage [11].

1.2 Star-like conjugated polymers

Functional polyhedral oligomeric silsesquioxane (POSS) is a class of large molecules containing an inorganic nanocage attached with organic groups, R (Fig. 1a). The contrast of electrochromic polymers can be improved by tethering conjugated polymer chains onto POSS nanocage as the star-like molecular architecture prohibits the dense packing of the rigid chains and hence greatly facilitates ion extraction and injection. With this approach, properties of electrochromic polymers may be tuned easily by the copolymerization of functional POSS with the wide variety of monomers that are available.

Cyclotriphosphazene (CP) is a non-delocalized cyclic ring consisting of alternating P and N atoms (Fig. 1b). Six organic functional groups, R, can be attached onto CP, which may be projected above and below the CP plane owing to their steric hindrance. Thus CP can also be used to synthesize star-like electrochromic polymers. Compared to POSS, the chemistry to synthesize functionalized CP is relatively straightforward. In addition, the CP ring is very stable and does not breakdown even under very aggressive chemical conditions.

Figure 1.1 Structures of (a) POSS and (b) CP.

1.3 Layer-by-layer (LbL) assembly of polymeric multilayer thin films

Polymeric electrochromic thin films are commonly fabricated via spin coating, spray coating or electropolymerization. Electrochromic thin films can also be prepared by a new assembly technology, LbL assembly. LbL assembly offers an inexpensive and easy processing technique for the creation of multilayer thin films. Different functional materials can be incorporated into the thin films with nanometer-sized control via LbL assembly. Many conjugated polymers have been fabricated into multilayer thin films successfully via LbL assembly and they exhibit high contrast and fast switching speed.

1.4 Motivation and objectives

The motivation for this study comes from the increasing demand for novel electrochromic materials with both high optical contrast and switching speed in visible range. The strategy used in this study is to use functional CP and POSS as a platform to synthesize novel star-like conjugated polymers, and to demonstrate that these novel polymers, combined with LbL film fabrication method, can provide both higher contrast and switching speed than conventional linear conjugated polymers. With the above motivation, the objectives of the study are:

- ❖ Study on the synergistic effect of star-like structure and LbL assembly technique on electrochromic properties.

- CP as core

- Study on the synthesis and electrochromic properties of dodecylbenzenesulfonic acid (DBSA) doped star-like hexa(4-aminophenoxy) cyclotriphosphazene-polyaniline (HACP-PANI) copolymers (HACP-PANI/DBSA).
- Study on the synthesis of star-like HACP-PANI in emeraldine base (EB) form (HACP-PANI-EB) and LbL assembly of HACP-PANI and poly(2-acrylamido-methane-2-propanesulfonic acid) (PAMPS), as well as electrochemical and electrochromic properties of HACP-PANI/PAMPS multilayer thin films.

- POSS as core

Study on the synthesis of star-like polyhedral oligomeric silsesquioxane-polyaniline (POSS-PANI) in EB form (POSS-PANI-EB) and LbL assembly of POSS-PANI and PAMPS, as well as electrochemical and electrochromic properties of POSS-PANI/PAMPS multilayer thin films.

- ❖ Study on the interaction mechanism of POSS-PANI and highly sulfonated polyaniline (SPANI) in multilayer thin films fabricated via LbL assembly and its effect on the electrochromic properties.

The scope of my Ph.D work (Fig. 1.2) is shown as follows,

Figure 1.2 The scope of my Ph.D work.

1.5 Organization of the thesis

Following this short introduction of Chapter 1, a review on electrochromic materials, electrochromic devices and applications, electrochromic performance parameters and characterization of electrochemical and electrochromic properties is presented in Chapter 2. Synthesis, characterization and electrochromic properties of HACP-PANI/DBSA copolymers are discussed in Chapter 3. Synthesis, LbL assembly and electrochromic properties of HACP-PANI/PAMPS multilayer thin films are reported in Chapter 4. Synthesis, LbL assembly and electrochromic properties of POSS-based star-

like polyaniline are reported in Chapter 5. High-contrast electrochromic thin films via LbL assembly of star-like and sulfonated polyaniline are reported in Chapter 6. The conclusions and recommendations are presented in Chapter 7.

2. LITERATURE REVIEW

2.1 Electrochromic materials

2.1.1 Electrochromism

Electrochromism first termed in 1961 by Platt [12] is the reversible and visible change in transmittance and/or reflectance in accompaniment with an electron-transfer or ‘redox’ reaction. It results from the generation of new or different visible region bands during the redox switching. The color change is commonly between a colored state and a bleached state. Some kinds of electrochromic materials can be said to possess multicolor-electrochromism or may be termed as polyelectrochromic if they have more than two redox states in accompaniment with the switch of several colors during electrochemical processes. This optical change is influenced by a small electric current at low dc potentials of the order of a fraction of volts to a few volts [13]. The first example of electrochromic materials and devices was demonstrated by Deb *et al.* [14] in 1969.

2.1.2 Types of electrochromic materials

2.1.2.1 Inorganic electrochromic materials

Transition metal oxides electrochromic materials are potentially useful due to their redox reactivity and intense coloration. Many transition metal oxides [15-26], such as iridium, tungsten, cobalt, manganese, nickel, palladium, cerium, rhodium, ruthenium, titanium, molybdenum, have been shown to possess electrochromic properties. This class of electrochromic materials has been classified under inorganic electrochromic materials. One of the most widely studied inorganic electrochromic materials is the tungsten trioxide

system (WO_3). WO_3 discovered by Deb [14] is a cathodically ion insertion electrochromic material. WO_3 , with all tungsten sites as oxidation state W^{VI} , is a transparent thin film. On electrochemical reduction, electrons transfer from one electrode to W^{VI} (reduction) to form some W^{V} centers and the color in the thin film of WO_3 change into blue (Eq. 2.1).

2.1.2.2 Organic electrochromic materials

I. Conjugated polymers

Conjugated polymers, which consist at least of one backbone chain of alternating single- and double-bonds, are organic macromolecules. In conjugated polymers, the p_z -orbitals of the carbon atoms which forms the π -orbitals of the alternating single and double bonds mesomerize more or less and double-bonds overlaps over the single bonds. Furthermore, conjugated polymers can be regarded as one-dimensional semiconductors because the π -electrons can be easily moved from one bond to the other. Similar to inorganic semiconductors, the conductivity of the conjugated polymers can be improved extremely by doping.

Chemical or electrochemical oxidation of many resonance-stabilized aromatic molecules, such as aniline, thiophene, azulene, pyrrole and others, produces electronically conjugated polymers. The repeat units of the common conjugated polymers are shown in Fig. 2.1.

Figure 2.1 The repeat units of the common conjugated polymers

II. Non-conjugated polymers and other organic compounds

Non-conjugated polymers which contain pendant π groups are significant to the field of electrochromics due to their ease of synthesis, processibility and tailorability [42]. Nishikitani *et al.* [43] synthesized two types of non-conjugated polymers derived from aromatic amine derivatives (DDP-A, DDB-P) (Fig. 2.3), both of which have a band gap in the ultraviolet region and are transparent and colorless in neutral states.

Besides non-conjugated conducting polymers, some organic compounds, such as para-benzoquinones, dichloro-dicyano-benzoquinone, fluoranil, benzoquinone and ortho-benzoquinones have also been studied as electrochromic materials [44].

Figure 2.3 The structures of DDP-A and DDB-P.

2.1.2.3 Hybrid materials

Hybrid materials [45-48] exhibit superior electrochromic properties compared with the pure conjugated polymers. Yu *et al.* [48] studied the electrochromic properties of poly[3-hexylthiophene-co-N-(3-trimethoxysilylpropyl) pyrrole] (P(3HT-co-3TPP))-silica hybrid materials. Their studies showed that P(3HT-co-3TPP)-silica hybrid materials had better electrochromic durability and adhesion. Xiong *et al.* [46] synthesized PANI-TiO₂ hybrids. PANI-TiO₂ showed the better long-term electrochromic stability, the higher coloration efficiency and optical contrast compared with PANI due to the covalent bond between TiO₂ and PANI, in which TiO₂ nano-domains act as electron acceptors and reduced the oxidation potential and band gap of PANI.

A new addition to the hybrid electrochromic materials are POSS-PANI, which has been introduced in Chapter 1.

2.1.2.4 Nanocomposites

The properties of organic/inorganic nanocomposites, such as mechanical strength, optical density, flexibility, and electrical and thermal conductivities, can be controlled by adjusting the compositions, nanophase size and chemical bonding between organic and inorganic materials. Many organic/inorganic nanocomposites [49-51] have been used in electrochromic devices and they exhibit higher optical contrast and faster switching speed compared with the pure components. Wu *et al.* [50] prepared water-soluble conducting poly(2-(3thienyloxy)ethanesulfonic acid) (PTOESA) (Fig. 2.4) /V₂O₅ nanocomposite. Compared with V₂O₅ and PTOESA, the nanocomposites show better optical contrast at the film thickness from 150 to 500 nm. During the oxidation process of (PTOESA)_xV₂O₅, the optical switching speed which was independent of the stoichiometry fell in between those of V₂O₅ and PTOESA. During the reduction process of (PTOESA)_xV₂O₅, the optical switching speed was less than those of V₂O₅ and PTOESA at high polymer content ($x > 0.5$). Baek *et al.* [51] reported that the optical contrast, switching speed and coloration efficiency of poly(1,4-bis(2-[3',4'-ethylenedioxy]thienyl)-2-methoxy-5-2''-ethylhexyl oxybenzene) (PBETH) (Fig. 2.4) /TiO₂ nanocomposites were improved significantly in comparison with that of the PBETH due to the interaction of PBETH with the TiO₂ nanoparticles.

Figure 2.4 The structures of PTOESA and PBETH.

2.1.2.5 Comparison between inorganic electrochromic materials and electrochromic polymers

A comparison between inorganic electrochromic materials and electrochromic polymers [13] was shown in Table 2.1.

Table 2.1 Comparison between inorganic materials and electrochromic polymers [13].

Properties		Inorganic materials	Electrochromic polymers
1	Preparation method for electrochromic thin film	Sophisticated techniques, such as electrodeposition, sputtering vacuum deposition, chemical vapour deposition	Simple techniques, such as spin-coating, spray-coating, electropolymerization, LbL assembly
2	Processibility	Poor processibility	Good processibility
3	Cost for electrochromic device	High cost	Low cost
4	Colors obtainable	Limited number of colors from a given material	Colors depend on the doping percentage, choice of the monomer, operating potential. Hence, plenty of colors are available with the polymeric materials
5	Contrast	Moderate contrast	High contrast
6	Switching speed	Slow	Fast
7	Life time	10^3 - 10^5 cycles	10^4 - 10^6 cycles

2.1.3 Typical electrochromic conjugated polymers

2.1.3.1 PANI

PANI is the most widely used anodically coloring electrochromic polymer. PANI are polyelectrochromic materials [52-54], which can show four kinds of different colors (yellow–green–blue–black) during its redox process. The color transition between yellow and green is repetitive color switching even though the leucoemeraldine form (yellow) is not conjugated. Four types of PANI from the fully reduced state (leucoemeraldine) to the fully oxidized state (pernigraniline) are shown in Fig. 2.5. Leucoemeraldine is an insulator because all rings are in benzenoid form and separated by $-NH-$ or $-NH_2^+-$ groups, which prevent the conjugation between rings. Emeraldine is either salt (ES) or EB

form, both of which has a ratio of one quinoidal ring to three benzenoid rings and are electrically conductive. Pernigraniline has equal proportions of quinoid and benzenoid moieties and exhibits metallic conductivity. Pernigraniline has an intense blue color and can appear black under very positive potentials if the film is thick enough.

yellow (leucoemeraldine)

green (emeraldine salt - conductor)

blue (emeraldine base)

black (pernigraniline)

Figure 2.5 Four types of PANI from the fully reduced (leucoemeraldine) to the fully oxidized (pernigraniline) forms. X^- is a charge-balancing anion.

PANI possesses good environmental stability and exhibits multicolor electrochromism in visible region as well as electrochromism in IR region. Many types of electrochromic devices based on PANI, such as PANI/ WO_3 [55, 56], PANI/PEDOT [57, 58], and PANI/Prussian blue (PB) [59] dual layer devices, have been reported, which demonstrated the great promise of PANI for electrochromic applications.

Since functionalization of conjugated polymers is an effective method to influence their electronic properties, conjugated polymers with various covalently attached functional

groups are of great interest in recent years. As electrochromic materials, the derivatives of PANI have excited considerable interest. Manisankar *et al.* [60] reported the synthesis and electrochromic properties of electroactive conducting copolymers of aniline and 4,4'-diaminodiphenyl sulfide (DDS). The copolymer film exhibited multicolor electrochromic behavior under different applied potential. At the concentration of 0.1 M DDS and 0.3 M aniline, the color of the copolymer can be changed from neutral yellow at 427 nm to green at 777 nm and to blue at 600 nm. The color changes from neutral yellow at 417 nm to dark green at 723 nm and to dark blue at 650 nm when the DDS concentration was 0.5 M. Huang *et al.* [61] electrochemically synthesized poly(2,5-dimethoxy aniline) (PDMA). When the applied potential was switched, PDMA showed reversible color changes from yellow to green, which represented the transition between reduced state to oxidized state. The coloration time of PDMA is 9 s and this value is much less than that of chemically prepared PANI (22 s).

2.1.3.2 PEDOT

PEDOT is the most widely used cathodically coloring electrochromic polymer, which has attracted much attention over the past 10 years. Its color can be switched between transparent, pale blue in oxidized state and dark blue in reduced state (Fig. 2.6). PEDOT [62] has a low band gap and oxidation potential for conversion to the conducting state and is very stable in the conducting form. Sindhu *et al.* [63] reported that the color of electropolymerized PEDOT film can be switched between deep blue and transparent blue. The response time of the device was 4.1 s, the contrast was nearly 35% and the ion storage capacity was 9.2 mC/cm². In order to enhance the contrast of PEDOT, a common approach is to increase the size of the alkylendioxy ring on PEDOT [10] or alter the size of the substituents attached to the ring [11] to enlarge the inter-chain distance, which

could effectively facilitate the diffusion of dopant ions and hence increase the contrast [12].

Figure 2.6 Electrochromic switching for PEDOT:PSS [64].

2.1.4 Doping

The conductivity of conjugated polymers can be improved significantly by the treatment with ionizing agents (charge-transfer agents). This process is termed ‘doping’. Between undoped and doped states of the conjugated polymers, the color change or contrast relies on the magnitude of the band gap of the undoped polymer. In the visible region, thin films of conjugated polymers with band gap greater than 3 eV (~ 400 nm) are transparent or colorless in the undoped form. In comparison, they are generally absorbing in the doped form. Those with band gap less than or equal to 1.5 eV (~ 800 nm) are highly absorbing in the undoped form. However, after doping, the free carrier absorption is relatively weak as it is transferred from the visible region to the near-IR (NIR). In

addition, the processibility of the conjugated polymers solution can be improved with acid doping. PANI doped with functionalized protonic acids, such as DBSA [65-70], diesters of sulfosuccinic acid [71] and Lewis acids [72], may be dissolved in weakly polar organic liquids. PEDOT is insoluble in solvents. The solubility problem of PEDOT has been solved with poly(styrene sulfonate) (PSS) used as a charge balancing counterion doping polymerization [73, 74]. At present, water-soluble PEDOT:PSS is commercially available.

2.2 Electrochromic devices and applications

Electrochromic devices can be divided into two categories: transmission electrochromic devices for the visible range and the reflective electrochromic device for the IR range.

2.2.1 Transmission electrochromic devices

Two kinds of transmission electrochromic devices can be used in the visible range. Fig. 2.7a illustrates the configuration of a single-layer electrochromic device with a sandwich structure [13, 75-78], from which the basic features and operating principles can be introduced conveniently. In the device, four layers are positioned between two substrates in a laminate configuration. Normally, the substrates are made of flexible polyester foil or glass. Conducting electrode layers, such as indium tin oxide (ITO)/fluorine-dope tin oxide, were coated on the substrates. The electrochromic materials can be spin-coated or spray-coated onto one of the conducting substrates. The electrochromic films can be turned into oxidized or reduced states by applying suitable potentials across the device, and the redox reaction is accompanied by a change in color. Another part of the four-layer construction is the electrolyte layer. During a redox process, the electrolyte layer functions as both an ionic conductor and a source or sink for ions' moving through the electrochromic material/electrolyte interface. The commonly used

electrolytes are gel electrolytes that can fall into two categories: polymer electrolytes and polyelectrolytes. Polymer electrolytes are comprised of neutral macromolecular species including poly(ethylene oxide) (PEO), poly(ethylene glycol) (PEG), poly(vinyl alcohol) (PVA) and poly(methyl methacrylate) (PMMA) within which salts such as LiClO_4 or LiCF_3SO_3 and acid H_3PO_4 , H_2SO_4 or HCl are dissolved in solvents to supply the mobile ions. Propylene carbonate (PC) or ethylene carbonate (EC) or mixed high boiling-point solvents are used as plasticizers. Polyelectrolytes are the polymers with ion-labile groups, such as PAMPS. In the past 30 years, gel electrolytes are the most widely used electrolytes for electrochromic devices owing to the relative ease of device fabrication. However, gel electrolytes do present some drawbacks which are difficult to overcome, such as thermal instability, toxic, solvent evaporation that can lead to insufficient conductivity. Recently, ionic liquids [79-82] have been employed to fabricate electrochromic devices. Ionic liquids are the salts that melt below $100\text{ }^\circ\text{C}$ and composed sole of cations and anions, such as 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{BMIM}][\text{PF}_6]$), 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{BMIM}][\text{BF}_4]$), 1-butyl-3-methylimidazolium bromide ($[\text{BMIM}][\text{Br}]$), 1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonimide ($[\text{BMIM}][\text{Tf}_2\text{N}]$), and 1-butyl-1-methylpyrrolidinium bis(trifluoromethane)sulfonimide ($[\text{BMPY}][\text{Tf}_2\text{N}]$). Compared with gel electrolytes, ionic liquids have many advantages, such as negligible vapor pressure, good thermal stability, wide liquid range and good conductivity. Ionic liquids can be used in many device fabrications such as electrochromic devices [81], lithium batteries [83], solar cells [84], fuel cells [85] and supercapacitors [86]. The main drawback of ionic liquid is leakage. In order to solve the problem, the blends of ionic liquids with polymeric ionic liquids [81] or other polymers such as poly(vinylidene fluoride)-hexafluoropropylene (PVDF-HFP) copolymer [87, 88] were used as the electrolyte layer. A summary about the electrolytes is shown in Table 2.2.

Figure 2.7 (a) A single-layer electrochromic device with a sandwich structure and (b) complementary electrochromic device.

Table 2.2 Organic electrolytes for use in electrochromic devices.

Electrochromic devices system	Electrolyte	Mobile Ion	Ref.
<i>Polymer Electrolytes</i>			
WO ₃	PMMA+EC+PC+LiClO ₄	Li ⁺	[55]
WO ₃	PVA + H ₃ PO ₄ /H ₂ SO ₄ /HCl	H ⁺	[89]
PEDOT-PSS	PEO+LiClO ₄	Li ⁺	[57]
PEDOT	PEO+LiCF ₃ SO ₃	Li ⁺	[90]
PANI	PMMA+EC+PC+LiClO ₄	Li ⁺	[91]
<i>Polyelectrolytes</i>			
PANI-WO ₃	PAMPS	H ⁺	[92]
PANI	PAMPS	H ⁺	[93]
WO ₃	PAMPS-PEO	H ⁺	[94]
<i>Ionic Liquids</i>			
PMeT and PEDOT	[BMIM]PF ₆	PF ₆ ⁻	[95]
PMeT, PHexT and POcT	[BMIM]PF ₆	PF ₆ ⁻	[96]
PEDOT/TiO ₂	[BMIM]BF ₄	BF ₄ ⁻	[82]
PEDOT	[BMIM]Br, [BMIM]BF ₄ [BMIM]PF ₆ , [BMIM]Tf ₂ N	Br ⁻ , PF ₆ ⁻ , BF ₄ ⁻ Tf ₂ N ⁻	[81]
CoHCF-PANI	[BMPY][Tf ₂ N]	Tf ₂ N ⁻	[97]

Complementary electrochromic device [95, 98-103] is another type of transmission electrochromic device (Fig. 2.7b). Compared with single-layer electrochromic device described above, one more layer of ion storage film, which normally is electrochromic

material, is positioned onto the other electrode. In the complementary electrochromic device, one electrochromic layer is cathodically colored and the other is anodically colored. Thus, the complementary electrochromic device can achieve higher contrast under the redox switching compared with the single-layer electrochromic device. In addition, the stability of the complementary electrochromic device is better than the single-layer electrochromic device because the charge produced by the oxidation reaction on one electrode can be depleted by the reduction reaction on the other electrode without any loss of materials in the complementary electrochromic device.

My Ph.D work is to study on the electrochromic properties in the visible range (400 nm ~ 800 nm). Thus, only transmission electrochromic devices are studied.

2.2.2 Reflective electrochromic device

Transmittance electrochromic devices cannot be used for IR modulation because of the high IR absorption of the electrolyte layer. Recently, Reynolds' research group [104-106] reported a kind of novel reflective electrochromic device utilizing a dual-polymer configuration (Fig. 2.8). In the device, an active electrochromic layer for the front working electrode (WE) was deposited onto a metallized porous membrane. The counter electrode (CE) was placed face up onto a transparent plastic substrate and a thin layer of gel electrolyte was homogeneously added. Then the membrane with the active electrochromic coating was placed, face-up, on the CE. Finally, several drops of gel electrolyte were added on top of the active layer to make sure the adequate swelling of the polymer. The reflective electrochromic device can be used to modulate the reflectivity in the visible, NIR, and mid-IR regions of the spectrum. Aubert *et al.* [104] reported the conjugated polymers of PEDOT, poly(3,4-propylenedioxythiophene) (PProDOT) and the dimethyl-substituted derivative PProDOT-Me₂ can achieve electrochromic contrast values of up to 90% in the NIR region and 60% in the visible regions and switching times

are 0.1-0.2 s to achieve full electrochromic contrast using the reflective electrochromic device. In addition, the reflective electrochromic device can be switched 180 000 times with less than 10% loss of contrast. Schwendeman *et al.* [105] reported that the electrochromic contrast of PProDOT-Me₂ as the active layer in the reflective electrochromic device is greater than 80% between 1.3-2.2 μm in the NIR and greater than 50% between 3.5-5.0 μm .

Figure 2.8 Reflective electrochromic device configuration [104].

2.2.3 Fabrication techniques for electrochromic devices

Polymeric electrochromic thin films can be fabricated via spin coating, spray coating or electropolymerization, which are simple and convenient methods to create thin films. Spin coating method can be used to create thin films on small substrates. Spray coating allows homogenous deposition of polymer films over large, non-uniform substrate surfaces. Electropolymerization can be used to create thin films on porous substrates. Electrochromic thin films can be prepared by a new assembly technology, LbL assembly (Fig. 2.9). The LbL assembly is a versatile processing technique introduced in the early 1990s by Decher [107]. Since then, there has been virtually an explosion in the amount of scientific literature in this research field. LbL assembly can create thin films of macromolecular complexes with nanometer-sized control. In the process of LbL assembly,

a thin film is grown up from a substrate by alternately exposing the ionized substrate to dilute aqueous solutions or dispersions of materials with opposite multivalent attractive affinities. During each exposure, one component deposits to overcompensate the surface affinity, which causes the reversal of that affinity and allows the deposition of a layer of opposite affinity. The most commonly employed LbL assembly interactions are electrostatic forces, via which multilayer thin films can be created in polyanion and polycation solutions.

Figure 2.9 Diagram of LbL assembly [108].

LbL assembled multilayer films are a kind of composites with two components inherent in the films and can be designed to practically provide any type of functional performance. In comparison with traditional thin film fabrication methods, the LbL approach allows the incorporation of many different functional materials into a single film at a full range of compositions without the issues of phase separation [109] and can create multilayer thin films with better mechanical property although it is time-consuming. Many polymeric electrochromic multilayer films, such as PANI/PAMPS [110, 111], PANI/PSS [112], PANI/poly(vinyl sulfonate) [112], triarylamine polymers/poly(choline methacrylate) [109], poly(ethylene imine)/PEDOT [74], poly(4-(2,3-dihydrothieno[3,4-*b*][1,4]-dioxin-

2-yl-methoxy)-1-butanesulfonic acid/poly(allylamine hydrochloride) [113], linear poly(ethylene imine) (LPEI)/PB [114] and poly(hexyl viologen) (PXV)/PEDOT [115], have been reported. The high contrast values of these thin films along with water-based processing have demonstrated the potentials of this technique in enhancing performance of electrochromic devices. In addition, this technique making use of the advantage of large surface area provided by nanomaterials overcomes the drawback of long switching time. Delongchamp *et al.* [116] prepared high-contrast electrochromic nanocomposites using LPEI and PB nanoparticles via LbL assembly. The electrochromic performance of thick LPEI/PB nanocomposites is superior to that of inorganic PB films with higher contrast and competitive switching speed. The performance and multifunctional quality of these nanocomposites have an important impact on electrochromic windows, flexible displays, and even biomedical devices.

2.2.4 Applications of electrochromic devices

The commercial applications [1, 4, 13, 15, 117] of electrochromic devices in visible range include the use of electrochromic windows in buildings, the use of rear-view mirrors in cars and the use of glare-reduction systems in offices. In addition, electrochromic materials can be used for protective eyewears, e-paper, spacecraft thermal control, displays, re-usable price labels, and controllable aircraft canopies. Some examples are shown in Fig. 2.10 [30, 118]. Besides their applications in visible range, electrochromic materials and their reflective electrochromic devices [15, 104, 105, 119, 120] have attracted high interest in response to the current need for devices optically active in IR range. When electrochromic materials can alter the IR emissivity, they can also be used for thermal emittance control, such as IR camouflage and space shuttles [5, 121]. A significant amount of information about the applications of electrochromic materials and electrochromic devices can be found on the related websites [122].

Figure 2.10 Electrochromic applications of (a) e-paper, (b) smart sunglasses [30] and (c) smart windows [118].

2.3 Electrochromic performance parameters

2.3.1 Electrochromic contrast

Electrochromic contrast [11, 123, 124] is probably the most important parameter to evaluate electrochromic materials. It is required to measure the intensity of the color change quantitatively in any electrochromic system. In transmissive mode, the optical absorbance (A) can be calculated using the following equation (Eq. 2.1).

$$A = \log\left(\frac{I_o}{I}\right) = \eta Q \quad (2.1)$$

In Eq. 2.1, I_o is the intensity of the light before it enters the sample or the intensity of incident light, I is the intensity of light at a specified wavelength which has passed through a sample, η is the ‘coloration efficiency’ of the electrochromic film and Q is the injected charge *per* unit area. The highest optical contrast of an electrochromic material under constant applied potentials is often reported as the maximum of the change in absorbance (ΔA) or the percent transmittance change ($\Delta\%T$) at a specified wavelength.

2.3.2 Switching speed

Switching speed is often reported as the time required for an electrochromic device to change between its colored state and bleached state. Normally, the switching speed for the coloration process and bleaching process are termed as coloration time and bleaching time separately. Quantification of the switching speed [114, 125] for an electrochromic device can be made by defining a change in 90% of the total absorbance span as indicating switching completion. Switching speed values are of the order of seconds for most of the electrochromic devices. The switching speed of an electrochromic material is related with several factors [126], such as the morphology and thickness of electrochromic materials, the ionic conductivity of the electrolyte, the magnitude of the applied potential and the accessibility of the ions to the electroactive layers.

2.3.3 Coloration efficiency

The coloration efficiency (η), which is a practical and efficient tool to measure the power requirements of electrochromic materials, can be calculated using the following equation (Eq. 2.2) [127].

$$\eta = \frac{\Delta A}{Q} = \frac{(\alpha d)}{Q} \quad (2.2)$$

In Eq. 2.2, ΔA is the optical absorbance change in the bleached state and colored state, Q is the charge *per* unit area, α is the linear absorption coefficient and d is the thickness of the electrochromic film. The coloration efficiency can be used to determine the amount of optical density change which is induced as a function of the injected/ejected electronic charge. The relationship between the charge injected to electrochromic materials and η is a practical parameter to evaluate the reaction coordinate of the coloration process compared with the charge injected to electrochromic materials [126, 128].

2.3.4 Cycle Life

The cycle life is the number of the cycles possible before the failure of the device. It is usually used to measure the stability of an electrochromic device. Cycle life is related to the electrochemical stability of an electrochromic device because the degradation of the active units during the redox switching leads to the loss of electrochromic contrast. Heat release due to the resistive parts in the system, side reactions due to the presence of oxygen or water in the cell or irreversible oxidation or reduction at extreme potentials can lead to the degradation of electrochromic materials [126]. The factors of defect-free processing of thin films, careful charge balance of the electroactive components, and air-free sealing of devices are very important and necessary for long-term operation of electrochromic devices.

2.4 Characterization of electrochemical and electrochromic properties

2.4.1 Electrochemical cell with three electrodes

The parameters of electrochromic materials can also be characterized in a cuvette filled with electrolyte solutions. In a typical three-electrode cell, the electrode onto which electrochromic materials were coated was used as the WE and a platinum or carbon wire was commonly used as the CE. Since there is typically not enough room in the cuvette to fit a real reference electrode (RE), and a pseudo-RE, such as silver wire, is usually employed. Pseudo-RE should be calibrated by spiking the electrolyte solution with a little amount of a well-behaved reversible redox species, such as potassium ferricyanide (for aqueous solutions) or ferrocene (Fc) (for nonaqueous solutions). The electrochemical cell is inexpensive, easy to clean and set up. Only a little amount of electrolyte solutions need to be used to complete the electrochemical experiments in the cuvette [129, 130]. The configuration of three-electrode electrochemical cell is shown in Fig. 2.11.

Figure 2.11 The configuration of three-electrode electrochemical cell in a cuvette.

2.4.2 Characterization methods

2.4.2.1 Cyclic voltammetry

Cyclic voltammetry (CV) is one of the most commonly used electrochemical techniques to measure the electroactivity of conjugated polymers. It is often used as a diagnostic tool to elucidate the potentials at which oxidation and reduction processes take place, the degree of reversibility of the electrode reactions and the potential range over which the electroactive materials coated on electrodes are stable. Thus, important parameters obtained from the CV curves of electroactive polymers include the potentials' value of the oxidation and reduction peaks, the dependence of peak current densities on scan rate or square root of the scan rate, the dependence of anodic-cathodic peak separation on scan rate, and half-wave potentials.

2.4.2.2 Chronoamperometry

In a chronoamperometric experiment, the current is monitored as a function of time when a large magnitude potential step is applied. Under a single potential step, the doping/dedoping process is close to finish in an electrochemical cell only if the current vs. time tends to be stable. Thus, in a spectroelectrochemical experiment, chronoamperometry is a simple and practical method for us to observe the time when the absorbance/transmittance spectra should be recorded.

2.4.2.3 Spectroelectrochemistry

Spectroelectrochemistry, which combines the electrochemical and spectroscopic techniques, has been used successfully to examine the optical changes that occur during the redox reactions in an electrochromic film. The technique can be used to probe structural changes and provide the information about electronic band modifications during the redox processes. Measurements were carried out with a UV-Vis

spectrophotometer and a potentiostat. Commonly, an electrochromic device or electrochemical cell were positioned in the sample compartment of the UV-Vis spectrophotometer and connected to a potentiostat to allow potentials' application while monitoring the transmission/absorption spectra [131]. According to the spectroelectrochemical plot, the contrast and the wavelength (λ_{max}) corresponding to the maximum change in absorbance (ΔA) under the constant applied potentials can be obtained.

2.4.2.4 Electrochromic switching study

Electrochromic switching study is another method to investigate spectroelectrochemically the kinetics of color change within electrochromic materials or devices by performing fast spectral scan at the single wavelength of λ_{max} while applying potential steps. This experiment can be used to quantitatively measure the contrast and switching speed under dynamic switching conditions. The experimental setup is the same as that for spectroelectrochemical measurements.

3. SYNTHESIS, CHARACTERIZATION AND ELECTROCHROMIC PROPERTIES OF DBSA-DOPED HACP-PANI COPOLYMERS

3.1 Introduction

Electrochromic contrast is one of the key performance indicators for an electrochromic material. As mentioned in Chapter 2, recently, significant contrast enhancement has been achieved by tethering PANI onto POSS nanocage to create a loosely packed structure with increased ionic conductivity [13]. CP is a non-delocalized cyclic ring, onto which six functional groups attached are normally projected above and below the CP plane due to steric hindrance [14]. Thus, when conjugated polymer chains are attached onto a CP ring, the molecules formed may possess star-like conformation similar to that of POSS-PANI, and the resultant materials may exhibit a loosely packed solid-phase structure resembling that found in POSS-PANI [15]. In addition, the versatility of cyclotriphosphazene chemistry and high stability of the CP ring allow a wide range of functional groups to be attached onto CP. It may thus provide an alternative route to enhance the contrast of various types of electrochromic polymers. In this chapter, the synthesis, characterization and electrochromic properties of PANI tethered CP to demonstrate the potential of this approach is reported. The relationship among crystallinity behavior, crystal size, ionic conductivity and their electrochromic properties of HACP-PANI copolymers is studied.

3.2 Experimental sections

3.2.1 Materials

Sodium hydrogen, *p*-nitrophenol, palladium-active carbon (10%), ammonium formate, DBSA, ammonium peroxydisulfate (APS), lithium perchlorate, acetonitrile (99.8%, anhydrous), PEG400 and PMMA ($M_w = 120000$ g/mol) were purchased from Aldrich Chemical Co. and used as received. Phosphonitrilic chloride trimer (Aldrich) was recrystallized in ethyl acetate and aniline (Aldrich) was purified by vacuum distillation prior to use. Tetrahydrofuran was freshly distilled over sodium/benzophenone before use. Other chemicals were obtained from various commercial sources and used as received.

3.2.2 Structural analysis

IR spectra were obtained on a PerkinElmer Fourier transform infrared (FTIR) spectrophotometer 2000 using KBr method. ^1H , ^{13}C and ^{31}P nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance-DRX-400 NMR spectrometer using deuterated dimethyl sulfoxide (*d*-DMSO) as solvent unless stated. Tetramethyl silane was used as an internal reference for ^1H and ^{13}C NMR spectra, and 85% H_3PO_4 was used as an external reference for ^{31}P NMR spectra. Mass spectra were obtained using a VG7035 mass spectrometer with electron-impact ionization. Elemental analysis was carried out with a PerkinElmer 2400 CHN and CHNS elemental analyzers. Size exclusion chromatography (SEC) was performed on a Waters 2690 equipped with a refractive-index detector using THF as an eluting solvent at a rate of 1.0 ml/min with polystyrene as the standard. Thin layer chromatographic analysis (TLC) was carried out on Polygram silica gel plates for UV_{254} with DMSO as the eluent.

3.2.3 Monomer synthesis

The synthesis routes for hexa(4-nitrophenoxy) cyclotriphosphazene (HNCP) and hexa(4-aminophenoxy) cyclotriphosphazene (HACP) are depicted in Scheme 3.1. They were prepared according to the reported procedures [132-135]. HNCP: Yield: 52.7%. ^1H NMR (δ , ppm): 7.31 (d, 2H, $J = 9.0$ Hz), 8.16 (d, 2H, $J = 9.0$ Hz). ^{13}C NMR (δ , ppm): 154.54, 145.78, 126.64, 122.37. ^{31}P NMR (δ , ppm): 8.41. IR (KBr, cm^{-1}): 1589, 1523, 1488, 1348, 1272, 1204, 1162, 1110, 950. Electron-impact mass spectrometry (EIMS) (m/z , percentage of relative intensity): 963.5 (M^+ , 38), 825.4 (100). ELEM. ANAL. Calcd. for $\text{C}_{36}\text{N}_9\text{O}_{18}\text{P}_3\text{H}_{24}$: C, 44.87; N, 13.08; H, 2.51. Found: C, 44.82; N, 12.97; H, 2.41. HACP: Yield: 89%. ^1H NMR (δ , ppm): 6.52 (d, 2H, $J = 8.7$ Hz), 6.43 (d, 2H, $J = 8.8$ Hz), 4.87 (d, 2H); ^{13}C NMR (δ , ppm): 146.41, 141.84, 121.78, 115.20; ^{31}P NMR (δ , ppm): 11.12. IR (KBr, cm^{-1}): 3437, 3413, 3343, 1624, 1498, 1263, 1174, 963. EIMS (m/z , percentage of relative intensity): 783.6 (M^+ , 33), 675.5 (100). ELEM. ANAL. Calcd. for $\text{C}_{36}\text{N}_9\text{O}_6\text{P}_3\text{H}_{36}$: C, 55.18; N, 16.09; H, 4.63. Found: C, 55.11; N, 15.94; H, 5.21.

Scheme 3.1 Synthesis of HACP.

3.2.4 Polymerization

HACP-PANI/DBSA were prepared by oxidative emulsion copolymerization [11] of HACP and aniline in the presence of DBSA with APS as the oxidizing agent, as shown in Scheme 3.2. The feed molar ratio of HACP to aniline was 0.5/99.5, 2.0/98.0 and 4.0/96.0, respectively. For clarity, the values of the HACP feed concentrations are specified in

sample names. In a typical reaction, aniline (1.86 g, 0.02 mol) and a designated amount of HACP were added into an emulsion prepared from deionized water (80 ml) mixed with DBSA (9.78 g, 0.03 mol) and xylene (24 ml) in a cooling bath maintained at 5 °C. Polymerization was initiated by the addition of APS (1.83 g, 0.008 mol) in deionized water (8 ml) over a period of 30 minutes. The total polymerization time was 24 hours. HACP-PANI/DBSA solutions were then obtained by extracting the emulsions with xylene. DBSA-doped PANI was prepared following the same procedure. HACP was also mixed with DBSA-doped PANI at the HACP/PANI molar ratio of 4/96 by solution blending in xylene without APS to provide a HACP/PANI physical blend as a reference material.

Scheme 3.2 Synthesis of HACP-PANI copolymers.

3.2.5 Device fabrication and characterization

The solutions of doped PANI, HACP/PANI blend and HACP-PANI copolymers in xylene were spin-coated onto ITO electrodes (60 Ω/□) laminated on poly(ethylene terephthalate) (PET) substrates, respectively, to form electrochromic layers. The film thickness was estimated by examination of the cross section of the cryogenically fractured samples using a JSM-6340F field-emission scanning electron microscope (FESEM), and the same instrument was also used to examine surface morphology of the electrochromic thin films. Electrochromic devices with a sandwich structure of PET-ITO|electrochromic

polymer|gel electrolyte|PET-ITO were then fabricated. The gel electrolyte was prepared by first dissolving PMMA (1.5 g, 0.0125 mmol) in dry acetonitrile (30 ml). LiClO₄ (0.5 g, 4.7 mmol) was then added into the solution. Finally, PEG400 (8 ml) was added. The mixture was stirred for 24 hours to form a homogeneous gel [90, 105, 136]. The in-situ spectroelectrochemical properties of the devices were characterized using an Autolab PGSTAT30 electrochemical workstation and ultra violet-visible (UV-vis) spectrophotometer (Shimadzu 5301). The workstation was also used to measure the ionic conductivity of the electrochromic layers in 0.3 M NaCl with Ag/AgCl (3M KCl) as RE and stainless steel as the CE. The impedance was determined at five discrete frequencies per decade over the range of 10⁴ to 10⁻² Hz with signal amplitude of 10 mV. The transmission-line model [137] was used for the impedance data analysis. A four-point probe system (Signatone SP4-62.5-85-TC) [138] was used to measure the surface electrical conductivity of the polymer films. Wide angle X-ray diffraction (WAXD) measurements were performed using a Shimadzu 6000 X-ray diffractometer with Cu K α radiation. All of the samples were scanned from 10° to 35° 2 θ . The thickness of the crystals were calculated using the Scherrer equation ($T = \frac{0.9\lambda}{FWHM \times \cos \theta}$) where λ is the X-ray wavelength, and FWHM the full width at half maximum in radians of the reflection at 2 θ . TEM images of the polymer thin films cast on a carbon-coated copper grid were obtained using a JEOL JEM-2100 high-resolution transmission electron microscopy (TEM) at an accelerating voltage of 200 kV.

3.2.6 Molecular simulation

The conformation of HACP was calculated via energy minimization using Materials Studio v3.1 (Accelrys software Inc., San Diego, USA). The Discover module was used in

the simulation that permits the use of different minimization algorithms (and a combination of them) to relax the system and minimize energy [139, 140].

3.3 Results and discussion

3.3.1 Chemical structure of the copolymers

Three HACP-PANI copolymers were prepared at the HACP feed concentration of 0.5 mol.%, 2.0 mol.% and 4.0 mol.%, respectively, and all were in situ doped with DBSA. The polymers can be dissolved well in xylene, which indicates that cross-linking did not occur substantially. The chemical structure of the copolymers was characterized using NMR and SEC. As an example, the ^{31}P NMR spectra of HACP and 4.0%HACP-PANI are shown in Fig. 3.1. A singlet at δ 10.11 is observed in the ^{31}P NMR spectrum of 4.0%HACP-PANI, which indicates that six PANI chains are covalently bonded onto a CP ring, making the three phosphorous atoms magnetically equivalent but have a different chemical environment from that in HACP. A question may arise that whether the singlet observed in the ^{31}P NMR spectrum of 4.0%HACP-PANI could originate from the complex of the unreacted starting material HACP with DBSA. TLC experiments were thus carried out to find out whether the extracted xylene solution contains any unreacted HACP. TLC results confirmed that no HACP could be detected in the xylene solution within the TLC detection limit, which unambiguously rules out the possibility that the singlet at δ 10.11 comes from HACP-DBSA complex. It further suggests that the xylene solution contains HACP-PANI copolymers rather than a physical mixture of HACP and PANI.

Figure 3.1 ^{31}P NMR spectra of (a) HACP and (b) 4.0%HACP-PANI copolymer.

Molecular weights and polydispersity of PANI and HACP-PANI copolymers measured by SEC using polystyrene as standard are summarized in Table 3.1. It shows that the molecular weights of the copolymers are significantly higher than that of homopolyaniline synthesized under the same condition, implying that large molecules with multiple PANI arms have been formed. It is worth noting that all six amine groups are located at para-position of phenyl rings in HACP, which enable PANI chains to grow from all six amine groups although the final arm length may be different. From SEC data, the number of repeat units in each arm is estimated to be 8, 10 and 9 by average for 0.5%HACP-PANI, 2.0%HACP-PANI and 4.0%HACP-PANI, respectively, while from the feed HACP/aniline molar ratio, the average arm lengths for 0.5%HACP-PANI, 2.0%HACP-PANI and 4.0%HACP-PANI should be 34, 9 and 5, respectively, based on the assumption that 100% conversion of HACP and aniline were achieved and no homopolymerization and cross-linking took place during the polymerization. The large deviation in the number of repeat units in each arm for 0.5%HACP-PANI indicates that a significant amount of homopolyaniline is formed at this low HACP concentration. The higher-than-expected molecular weight for 4 mol.% HACP implies that cross-linking may occur to some extent at high HACP concentrations.

Table 3.1 SEC results of PANI and HACP-PANI copolymers.

Sample	HACP/aniline molar ratio	Molecular weights		
		M_n	M_w	$PDI = M_w/M_n$
PANI	0/100	3152	3178	1.01
0.5%HACP-PANI	0.5 / 99.5	5063	6289	1.24
2.0%HACP-PANI	2.0 / 98.0	5970	7881	1.32
4.0%HACP-PANI	4.0 / 96.0	5292	6512	1.23

3.3.2 Spectroelectrochemical characterization

The UV-vis absorption curves of the electrochromic devices with PANI and HACP-PANI copolymers as the electrochromic layer, respectively, at different potentials are shown in Fig. 3.2. Both PANI and HACP-PANI copolymers could be switched between a relatively transmissive reduced state (greenish yellow) and absorbing oxidized states (green and blue). In order to make a fair comparison, the thickness of the electrochromic layers was controlled to be consistent among all samples. When switched from -2.0 to $+2.0$ V, the contrast of 0.5%HACP-PANI and 2.0%HACP-PANI copolymers at λ_{max} are lower than that of PANI. Only when HACP concentration is 4.0 mol.%, the maximum change in absorbance of the copolymer at its λ_{max} is significantly higher than that of PANI. In contrast, when 4.0 mol.% HACP is physically mixed with PANI by solution blending, the contrast of the blend is about the same as that of PANI, which indicates that the increase in electrochromic contrast observed from 4.0%HACP-PANI is brought by the covalent bonding of PANI chains to CP.

Figure 3.2 Visible spectra of the electrochromic devices with (a) PANI, (b) 0.5%HACP-PANI, (c) 2.0%HACP-PANI, (d) 4.0%HACP-PANI and (e) HACP/PANI blend (4.0 mol. % HACP) as the electrochromic layers, respectively, at different potentials (-2.0 , -1.0 , 0.0 , $+1.0$, $+2.0$ V).

3.3.3 Electrochromic switching studies

The optical switching behaviors of the devices were also examined at their λ_{max} with the potential stepped between -2.0 V and $+2.0$ V at 20 s per cycle (Fig. 3.3). It is clear that the contrast of 4.0%HACP-PANI ($\Delta A = 0.212$) is also higher than that of PANI ($\Delta A = 0.167$) under dynamic conditions. The relatively high contrast achieved with 4.0%HACP-PANI can be attributed to the loose packing of PANI chains in 4.0%HACP-PANI brought by its star-like conformation (Fig. 3.4), which hinders ordered packing and thus allows facile ion motion during the redox switching. The coloration time of 4.0%HACP-PANI (6.7 s) is close to that of PANI (7.0 s). The reduced contrasts for 0.5%HACP-PANI and 2.0%HACP-PANI are related to the unique crystallization behavior of HACP-PANI copolymers, as discussed in the next section.

Figure 3.3 Optical switching for the devices with 4.0%HACP-PANI and PANI as electrochromic layers separately, under square-wave potentials oscillating between -2.0 and $+2.0$ V.

Figure 3.4 Conformation of HACP with minimized potential obtained from molecular dynamics simulation.

3.3.4 Crystallization of the copolymers

WAXD patterns of HACP, PANI, and HACP-PANI copolymers are shown in Fig. 3.5a. It is obvious that the WAXD patterns of the copolymers are different from that of HACP but closely resemble that of PANI, which indicates that it is PANI chains that crystallize. All polymer samples exhibit two distinctive diffraction peaks at about 21.2° and 24.8° 2θ , which somewhat resemble that of EBII-ESII [141]. The intensities of the X-ray peaks of 0.5% HACP-PANI are much higher than that of PANI, which implies that the inclusion of CP induces the crystallization of PANI. As mentioned earlier, the polymerization products are mixtures of homopolyaniline and HACP-PANI copolymers at low HACP concentrations. As the HACP concentration increases, the homopolyaniline content decreases. The crystallinity, as estimated from X-ray peak intensities, thus decreases. When HACP concentration reaches 4.0 mol.%, the crystallinity becomes slightly lower than that of PANI as the content of homopolyaniline in the solution is very low. The crystal thickness of PANI and HACP-PANI copolymers estimated from the FWHM of

the strongest X-ray peak in the spectra using Scherrer equation was also plotted against HACP concentration (Fig. 3.5b). It shows the same trend as the crystallinity.

Figure 3.5 (a) X-ray diffraction patterns and (b) crystal thickness estimated from FWHM of the copolymers.

The morphologies of the polymer thin films were examined using FESEM (Fig. 3.6). Stripy features, which are likely to be crystalline regions, could be observed from PANI, 0.5%HACP-PANI and 2.0%HACP-PANI, with the two copolymers showing a high population of long strips while PANI showing only some shorter strips. In contrast, such stripy features could hardly be observed from 4.0%HACP-PANI. A large number of nanometer-sized crystalline domains still, however, exist in 4.0%HACP-PANI, as indicated by the crystal lamellae observed via TEM (Fig. 3.7).

Figure 3.6 FESEM images of (a) PANI, (b) 0.5%HACP-PANI, (c) 2.0%HACP-PANI and (d) 4.0%HACP-PANI.

Figure 3.7 A TEM image of 4.0%HACP-PANI.

An important finding from the above experimental data is that the trend for crystallinity, crystal thickness and morphology is consistent with the trend for the optical contrast presented in Fig. 3.2. When HACP concentration is low (0.5 mol. % and 2.0 mol. %), the ion diffusion becomes more difficult due to the relatively high crystallinity and large crystal size, thus resulting in a low contrast. When HACP concentration is high (4.0 mol %), the crystallinity and crystal size are reduced and a loosely packed structure is formed. Such structural feature enables HACP-PANI to produce more accessible doping sites, which subsequently makes ion motion easier during the redox switching and thus leads to an increase in electrochromic contrast. The above claim is also supported by the ionic conductivity data shown in Fig. 3.8. 4.0%HACP-PANI shows the highest ionic conductivity among all samples.

Figure 3.8 Ionic and electrical conductivity of PANI and HACP-PANI copolymers.

It is, however, intriguing to see that although the crystal thickness of 4.0%HACP-PANI is comparable to that of PANI and the crystallinity of 4.0% HACP-PANI is slightly lower

than that of PANI, the electrical conductivity of 4.0%HACP-PANI is actually higher than that of PANI. This is opposite to the trend observed from DBSA-doped POSS-PANI (POSS-PANI/DBSA), where the increase in ionic conductivity by an order of magnitude brought by the loosely packed structure of POSS-PANI is accompanied by a decrease in electrical conductivity by an order of magnitude [11]. Moreover, for HACP-PANI copolymers, the electrical conductivity increases with increasing HACP concentration. A plausible explanation for this is that in some HACP-PANI molecules, the flexible ether linkage between the PANI chains and CP ring may rotate to cause two adjacent chains parallel to each other, which is driven by the strong interactions between rigid conjugated chains. The electrons may thus transfer more easily between the adjacent chains in HACP-PANI copolymers. The observed nucleating effect of HACP-PANI at low HACP concentrations supports the proposed mechanism.

3.4 Conclusions

In summary, the synthesis of electrochromic HACP-PANI copolymers has been readily achieved by emulsion polymerization and their chemical structures were characterized by various methods. Although the HACP-PANI copolymers with low HACP concentrations show a relative low electrochromic contrast with respect to homopolyaniline, the electrochromic contrast of 4.0%HACP-PANI is significantly improved due to its loosely packed structure and small crystal size, which led to a considerable increase in ionic conductivity and, as a result, more effective doping. Therefore, the introduction of a CP core covalently into electrochromic polymers at an appropriate molar percentage would offer an alternative way to enhance the electrochromic contrast of certain conjugated polymers.

4. SYNTHESIS, LBL ASSEMBLY AND ELECTROCHROMIC PROPERTIES OF HACP-PANI/PAMPS MULTILAYER THIN FILMS

4.1 Introduction

In Chapter 3, it has been demonstrated that although the electrochromic contrast of 4%HACP-PANI/DBSA copolymer is higher than that of PANI/DBSA, the switching speed of 4%HACP-PANI/DBSA is not improved significantly. This phenomenon was also found in POSS-PANI/DBSA copolymers [142]. The reason may be that a large amount of DBSA has occupied the space among the chains of HACP-PANI copolymers and POSS-PANI copolymers, inhibiting the ions' injection and extraction (Fig. 4.1). In order to get rid of the effect of excessive external doping acid on switching speed, the synthesis and characterization of HACP-PANI-EB, the combination of HACP-PANI with linear PAMPS to form multilayer thin films via LbL assembly, and the characterization of electrochemical and electrochromic properties of the multilayer thin films were carried out. The results are reported in this chapter.

Figure 4.1 The possible configurations of (a) HACP-PANI/DBSA and (b) POSS-PANI/DBSA.

4.2 Experimental section

4.2.1 Materials

Aniline, acetonitrile (99.5%), ammonium hydroxide solution (28.0-30.0% NH_3 basis), DMAc ($\geq 99\%$), PAMPS (aqueous 15wt. % solution, $M_w = \sim 2\,000\,000$), lithium perchlorate ($\geq 95.0\%$) and Fc (98%) were purchased from Aldrich. Aniline was purified by vacuum distillation prior to use. APS was purchased from Lancaster. Hydrochloric acid (HCl) was purchased from Honeywell. HNCP and HACP were synthesized according to the reported procedures [132-135]. Nylon filters ($0.45\,\mu\text{m}$, 150 ml) were purchased from Nalgene. Other chemicals were obtained from various commercial sources and used as received.

4.2.2 Preparation of HACP-PANI-EB

HACP-PANI copolymer was prepared by oxidative copolymerization [52, 143, 144] of HACP and aniline in the presence of HCl with APS as the oxidizing agent. In the reaction, aniline (3.72 g, 0.04 mol) and HACP (1.305 g, 1.7 mmol) were added into 1.2 M HCl (400 ml) in a cooling bath maintained at $0\,^\circ\text{C}$ for 4 h. Polymerization was initiated by the addition of APS (9.12 g, 0.04 mol) dissolved in 1.2 M HCl (200 ml) over a period of 30 min. The total polymerization time was 24 h. When the reaction was completed, the precipitated HACP-PANI copolymer in ES form (HACP-PANI-ES) was filtered and washed with 1.2 M HCl, distilled water and methanol. The collected powder was dried at $35\,^\circ\text{C}$ for 48 h under dynamic vacuum. HACP-PANI-EB was obtained by treating the HACP-PANI-ES with ammonium hydroxide solution [145]. The freshly prepared HACP-PANI-ES were suspended with constant stirring in ammonium hydroxide solution and stirred for 20 h. After that, the powder was collected and washed with fresh ammonium hydroxide solution. The washing process was repeated three times. The color

of the HACP-PANI-EB obtained is brown. PANI in EB form (PANI-EB) homopolymer was prepared using a procedure similar to that described above.

4.2.3 Structural analysis

Infrared spectra were obtained on a PerkinElmer FTIR spectrophotometer 2000 using KBr method. X-ray photoelectron spectroscopy (XPS) experiments were performed using a VG ESCALAB 220i-XL instrument equipped with a monochromatic Al K α X-ray source (1486.7 eV photons). The binding energy (BE) of the core level C 1s peak was set at 285.0 eV to compensate for surface-charging effects.

4.2.4 Preparation of dipping solutions

HACP-PANI-EB was dissolved in DMAc at a concentration of 10 mg/ml by first stirring the solution overnight and then sonicating it for about 8 h. Some indiscernible particulates were removed using centrifuge. The dipping solution was prepared by slowly adding one part (by volume) of the centrifuged HACP-PANI-EB solution to nine parts of water that has had its pH adjusted to about 3.0-3.5 with 1 M HCl. The pH value was then quickly lowered to 2.5 by adding drops of 1 M HCl solution. The solution was filtered through a 0.45 μ m Nylon filter just before use [110, 146]. The dipping solution containing PANI was prepared using the same procedure. The concentration of both PANI and HACP-PANI in the dipping solutions was adjusted to 0.04 mg/ml. PAMPS solution (2 mM) was prepared by dissolving the PAMPS in water under stirring and the pH value of the PAMPS aqueous solution was also adjusted to 2.5. The solution was filtered using filter paper before use.

4.2.5 LbL assembly of multilayer thin films

Multilayer thin films were constructed using a modified Carl Zeiss DS50 programmable slide stainer. Glass coated with ITO (5-15 $\Omega/\square$) and uncoated glass substrates, both with

the dimensions of $7 \times 50 \times 0.7$ mm (Delta Technologies) were cleaned by ultrasonication in a series of solvents including dichloromethane, acetone, methanol, and Milli-Q water at 15 minutes each, followed by a 4-minute air plasma cleaning (Harrick PDC 32G). Silicon wafers were treated in the plasma cleaner to provide a hydrophilic surface. ITO-glass, uncoated glass and silicon substrates were exposed first to polycation solution for 5-20 min, followed by three consecutive rinsing steps (1.5 min, 1.5 min, 1.5 min) in MilliQ water, then exposed to polyanion solution for 5-20 min and rinsed. The cycle was repeated to create multilayer thin films of certain thickness [111]. The pH value of all the rinsing solutions was adjusted to 2.5.

4.2.6 Thin film characterization

Thickness measurements were performed with a Tencor P16 profilometer. The XPS experiment is the same as reported before. The surface morphology of the thin films was examined using a JSM-6700F FESEM. In-situ spectroelectrochemical properties of the multilayer thin films were characterized using an Autolab PGSTAT30 electrochemical workstation and Cary UV-Vis-NIR spectrophotometer 6000i. The electrochromic thin films on ITO-glass as WE were positioned in a quartz cell with electrolyte. The electrolyte is 0.1 M LiClO₄ in acetonitrile. Platinum wire (99.99%) and silver wire (99.9%) were used as CE and RE respectively. The pseudo-RE wire was calibrated vs. Fc/Fc⁺ by dissolving Fc in the electrolyte solution and determining the $E_{1/2}$ of the Fc/Fc⁺ against the silver wire.

4.3 Results and discussion

4.3.1 Synthesis and structural verification

The HACP-PANI copolymer was prepared by oxidative copolymerization of HACP and aniline, as shown in Scheme 4.1. The feed molar ratio of HACP to aniline was

4.0/96.0. For clarity, the value of the HACP feed concentration is specified in sample names.

Scheme 4.1 Oxidative copolymerization of HACP and aniline to form HACP-PANI-ES, followed by conversion to HACP-PANI-EB.

The chemical structures of the PANI-EB homopolymer and 4%HACP-PANI-EB copolymer are characterized using FTIR and XPS. Comparing the FTIR spectra of HACP (Fig. 4.2a) with PANI (Fig. 4.2b) and 4%HACP-PANI (Fig. 4.2c), it is obvious that the strong characteristic peaks in 4%HACP-PANI-EB are from PANI rather than from HACP itself and these characteristic bands observed are associated with EB form of PANI [147, 148]. The band at 1585 cm^{-1} is attributable to C=C bonds of quinoid units and the band at 1493 cm^{-1} to C-C bonds of benzenoid units. The presence of the quinoid rings is also confirmed by the moderate band at 1155 cm^{-1} , which is related to the electronic-like absorption of N=Q=N vibration. The band corresponding to C-H out-of-plane bending of the 1,4-disubstituted aromatic ring appears at 826 cm^{-1} , which is the evidence for the formation of poly(*p*-aniline). Comparing the FTIR spectra of the 4%HACP-PANI-EB and the linear PANI-EB, there are a strong, broad absorption band at 947 cm^{-1} and a weak peak band at 1191 cm^{-1} only seen in the former. The peak at 947 cm^{-1} is attributable to P-O-C symmetrical stretching of CP and the peak at 1191 cm^{-1} is attributable to P-N-P asymmetrical stretching of CP. In view that the unreacted HACP is soluble in the acidic solution and would not precipitate out to form a part of the product, the appearance of P-O-C stretching band indicates that PANI-EB chains have been successfully tethered

onto the HACP core, which is also supported by XPS data from 4%HACP-PANI found (Fig. 4.3). In XPS of 4%HACP-PANI-EB, there is the characteristic peak of P 2p. The occurring of the peak demonstrated that polyaniline chains had been tethered onto the CP core. The characteristic peak of P 2p of 4%HACP-PANI-EB in powder form is sharper than that of HACP in powder form, which means the surface charging is decreased due to the conductivity of polyaniline chains tethered onto CP core. In addition, the characteristic peaks of P 2p of 4%HACP-PANI shift to the lower banding energy due to the long polyaniline chains.

Figure 4.2 FTIR spectra of (a) HACP, (b) PANI-EB and (c) 4%HACP-PANI-EB.

Figure 4.3 XPS P 2p of (a) HACP and (b) 4%HACP-PANI-EB.

4.3.2 LbL assembly of multilayer thin films

The homogeneity of LbL-assembled films can be affected by the surface treatment of substrates, pH values and concentration of polymer solutions. Thus, the study on the relationship between the dipping time of the substrates in polymer solutions and the absorbance of polymers adsorbed on substrates is very necessary in order to form homogeneous thin films. The time-dependent adsorption behavior (Fig. 4.4) of PANI/PAMPS and 4%HACP-PANI/PAMPS multilayer films shows that the spontaneous adsorption of polyaniline occurs very rapidly. The time to reach approximately complete adsorption takes about 15 minutes.

Figure 4.4 Plots of absorbance of the PANI/PAMPS and 4%HACP-PANI/PAMPS multilayer films (5 bilayers) adsorbed on glass substrates as a function of dipping time.

According to the time-dependent adsorption behavior of the PANI/PAMPS and 4%HACP-PANI/PAMPS adsorbed onto glass substrates, the dipping time in polycation and polyanion solution is optimized at 15 min. Fig. 4.5a shows that the LbL growth of PANI/PAMPS and 4%HACP-PANI/PAMPS multilayer thin films are linear [149] with the thickness of each bilayer being about 2.2 nm. The LbL assembled thin films are fairly homogenous as demonstrated by their uniform color (Fig 4.5b).

Figure 4.5 (a) Growth curves for LbL assembled PANI/PAMPS and 4%HACP-PANI/PAMPS thin films on glass and (b) a photograph of (4%HACP-PANI/PAMPS)₄₅.

Figure 4.6 (a) P 2p XPS spectrum of (4%HACP-PANI/PAMPS)_{15.5} on silicon wafer and (b) comparison of the P 2p XPS spectra of 4%HACP-PANI-EB and (4%HACP-PANI/PAMPS)_{15.5} thin films on silicon wafer.

Fig. 4.6 shows the XPS spectrum of 4%HACP-PANI measured from a (4%HACP-PANI/PAMPS)_{15.5} thin films on silicon substrate. A characteristic peak of P 2p is visible

in the spectrum, which verifies that 4%HACP-PANI copolymer has been successfully incorporated into the multilayer film. $(\text{PN})_3$ core is a non-delocalized cyclic ring consisting of alternating P and N atoms. CP core is very stable. As shown in Fig. 4.6b, there is no peak shift of P 2p peaks by comparing 4%HACP-PANI-EB in powder form and $(4\%\text{HACP-PANI/PAMPS})_{15.5}$ thin film, indicating that PAMPS has little effect on the electron density of the $(\text{PN})_3$ core, thus leading to no change in binding energy of P 2p in 4%HACP-PANI/PAMPS when compared with 4%HACP-PANI-EB. In addition, the XPS P 2p peak of 4%HACP-PANI-EB is clearer than that of 4%HACP-PANI/PAMPS thin films because the P concentration in 4%HACP-PANI-EB is much higher than that in $(4\%\text{HACP-PANI/PAMPS})_{15.5}$ multilayer thin films.

4.3.3 CV studies

Based on the growth curve presented in Fig. 4.5a, 45 bilayers of PANI/PAMPS and 4%HACP-PANI/PAMPS are assembled on ITO-coated glass. Both of the thin films have the same thickness of 100 nm, which allows a fair comparison of the electrochromic properties. The two thin films are named as $(\text{PANI/PAMPS})_{45}$ and $(4\%\text{HACP-PANI/PAMPS})_{45}$, respectively. The CV curves of both $(\text{PANI/PAMPS})_{45}$ (Fig. 4.7a) and $(4\%\text{HACP-PANI/PAMPS})_{45}$ (Fig. 4.7b) show two oxidation and reduction peaks. The first oxidation peak at lower potentials can be assigned to the leucoemeraldine to emeraldine transition, and the second oxidation peak at higher potentials is due to the transition from the emeraldine to pernigraniline state [58, 150]. Compared with linear PANI, PANI chains are better separated in HACP-PANI at the molecular level that allows for easier access of dopants to the electroactive sites, making the oxidation and reduction peaks of 4%HACP-PANI more distinctive.

Figure 4.7 CV curves of (a) (PANI/PAMPS)₄₅ and (b) (4.0%HACP-PANI/PAMPS)₄₅ measured in a 0.1 M LiClO₄/acetonitrile solution with scan rate of 10, 25, 50, 75 and 100 mV/s, respectively, using silver wire as the reference electrode.

4.3.4 Spectroelectrochemical characterization

Fig. 4.8 show series of UV-Vis absorbance spectra of (PANI/PAMPS)₄₅ and (4%HACP-PANI/PAMPS)₄₅ under different applied potentials varying from -0.3 V to $+0.9$ V vs. Fc/Fc⁺. PANI and 4%HACP-PANI can be switched between a relatively transmissive reduced state (yellowish green) and an absorbing oxidized state (blue). The maximum change in absorbance of (PANI/PAMPS)₄₅ ($\Delta A = 0.202$ at 626 nm) (Fig. 4.8a) is similar to that of (4%HACP-PANI/PAMPS)₄₅ ($\Delta A = 0.222$ at 620 nm) (Fig. 4.8b). Without applying potential, the intensity of the absorption peaks for PANI and 4%HACP-PANI are almost equivalent (Fig. 4.8c), which implies that the content of the active units in 4%HACP-PANI is nearly the same as that in PANI.

Figure 4.8 Visible spectra of (a) (PANI/PAMPS)₄₅ and (b) (4%HACP-PANI/PAMPS)₄₅ under different potentials (−0.3, 0, +0.2, +0.3, +0.5, +0.7, +0.9 V). (c) UV-Vis-NIR spectra of (PANI/PAMPS)₄₅ and (4%HACP-PANI/PAMPS)₄₅.

4.3.5 Electrochromic switching studies

The optical switching behaviors of the multilayer films are examined at λ_{max} using an UV-Vis spectrophotometer with the applied potential stepped between −0.3 V and +0.9 V at 40 s per cycle. It is obvious to see that the contrast of (4%HACP-PANI/PAMPS)₄₅ ($\Delta A = 0.128$) is significantly much lower than that of (PANI/PAMPS)₄₅ ($\Delta A = 0.156$) (Fig. 4.9). The switching kinetics of (4%HACP-PANI/PAMPS)₄₅ is not improved compared with (PANI/PAMPS)₄₅. The morphology and structure of the films have an important effect on ions transfer through the multilayer films and the dynamic redox

switching behaviors. Thus, in order to understand the reason why the contrast of $(4\%\text{HACP-PANI/PAMPS})_{45}$ is approximately the same as that of $(\text{PANI/PAMPS})_{45}$ under constant applied potentials, whereas they are very different under dynamic switching, it is necessary to compare the morphology of PANI and 4%HACP-PANI in the multilayer thin films.

Figure 4.9 Optical switching for $(\text{PANI/PAMPS})_{45}$ and $(4\%\text{HACP-PANI/PAMPS})_{45}$ with 100 nm thickness.

4.3.6 Surface morphology

The surface morphologies of the multilayer films with the electrochromic layer on top were examined using FESEM [151]. In Fig. 4.10a, the islands (bright regions) are separated by dark regions of several nanometers wide. In contrast, in Fig. 4.10b, it is obvious relatively a continuous layer formed. It has been shown before that PANI is tethered onto CP core by O linkage in HACP-PANI copolymer, in which the O atoms are very flexible due to its sp^3 hybrid orbits. Thus, the PANI chains in the HACP-PANI copolymer can rotate around O atoms. Because the PANI chains in polycation solutions is

4.4 Conclusions

In summary, 4%HACP-PANI-EB copolymer has been readily synthesized and their chemical structures verified by FTIR and XPS. 4%HACP-PANI/PAMPS multilayer thin films have been successfully fabricated via LbL assembly. Although the electrochromic contrast of (PANI/PAMPS)₄₅ and (4%HACP-PANI/PAMPS)₄₅ is similar under constant applied potentials, the contrast of (4%HACP-PANI/PAMPS)₄₅ is much less than that of (PANI/PAMPS)₄₅ under dynamic switching and the switching kinetics of (4%HACP-PANI/PAMPS)₄₅ is not improved compared with (PANI/PAMPS)₄₅. The reason may be HACP-PANI with flexible -O- linkage between CP and PANI exhibits a planar structure in LbL-assembled films and hence gives rise to a dense packing structure.

5. SYNTHESIS, LBL ASSEMBLY AND ELECTROCHROMIC PROPERTIES OF POSS-BASED STAR-LIKE POLYANILINE

5.1 Introduction

In Chapter 4, it has been verified that the HACP-PANI can be fabricated into multilayer thin films via LbL assembly successfully. However the contrast of (4%HACP-PANI/PAMPS)₄₅ is much less than that of (PANI/PAMPS)₄₅ under dynamic switching because of its densely packed structure. In order to make use of star-like core to create loosely packed structure and get rid of the flexible -O- linkage between the core and PANI, OAPS was selected as the core of star-like conjugated polymers. The comparison between OAPS and HACP is shown in Table 5.1. The aniline groups are directly linked to the nanocage in OAPS while the aniline groups are linked to the CP ring by the O linkage in HACP.

In this chapter, the synthesis and characterization of POSS-PANI-EB, the combination of POSS-PANI-EB with linear PAMPS polyanion to form multilayer thin films via LbL assembly, and the electrochemical and electrochromic properties of POSS-PANI/PAMPS multilayer thin films are reported. Furthermore, a clear comparison about the electrochromic properties of LbL assembled POSS-PANI/PAMPS with PANI/PAMPS and LbL assembled POSS-PANI/PAMPS with spin-coated electrochromic thin film of POSS-PANI/polymeric acid complexes is provided.

Table 5.1 Comparison of OAPS and HACP.

Materials	Star-like core	The linkage between aniline groups and core
OAPS		rigid linkage
HACP		flexible O linkage

5.2 Experimental Section

5.2.1 Materials

Octa(aminophenyl) silsesquioxane (OAPS) was purchased from Mayaterials Inc. and purified to reduce the content of octa(nitrophenyl) silsesquioxane prior to use. Triethylamine was purchased from Lancaster. Other chemicals are the same as reported in Chapter 4.

5.2.2 Preparation of POSS-PANI-EB

POSS-PANI copolymers were prepared by oxidative copolymerization [143, 144] of OAPS and aniline in the presence of HCl with APS as the oxidizing agent. In a typical reaction, aniline (3.72 g, 0.04 mol) and OAPS (0.47 g, 0.40 mmol) were added into 1.2 M HCl (400 ml) in a cooling bath maintained at 0 °C for 4 h. Polymerization was initiated by the addition of APS (9.12 g, 0.04 mol) dissolved in 1.2 M HCl (200 ml) over a period of 30 min. The total polymerization time was 24 h. When the reaction was completed, the

precipitated POSS-PANI copolymer in ES form (POSS-PANI-ES) was filtered and washed with 1.2 M HCl, distilled water and methanol. The collected powder was dried at 35 °C for 48 h under dynamic vacuum. POSS-PANI-EB was obtained by treating the POSS-PANI-ES with triethylamine solution [145], which was diluted using anhydrous chloroform. The freshly prepared POSS-PANI-ES were suspended with constant stirring in triethylamine solution and stirred for 20 h. After that, the powder was collected and washed with anhydrous chloroform. The washing process was repeated three times. The color of the POSS-PANI-EB obtained is dark brown. The PANI-EB homopolymer was prepared using a procedure similar to that described above. PSS-doped POSS-PANI copolymer (1%POSS-PANI/PSS) was synthesized according to the reported procedure [152].

5.2.3 Structural analysis

Infrared spectra were obtained on a PerkinElmer FTIR spectrophotometer 2000 using KBr method. Elemental analysis was carried out with a PerkinElmer 2400 CHN and CHNS elemental analyzers.

5.2.4 Preparation of dipping solutions and LbL assembly of multilayer thin films

The preparation method for POSS-PANI (polycation), PAMPS (polyanion) solutions and the LbL assembly of the multilayer thin films are the same as reported in Chapter 4.

5.2.5 Thin film characterization

Atomic force microscope (AFM) measurements were performed in the tapping mode using Digital Instruments Nanoscope 3100 AFM. Thickness measurement, XPS experiments, surface morphology characterization and the electrochemical experiments are the same as reported in Chapter 4.

5.3 Results and discussion

5.3.1 Synthesis and structural verification

POSS-PANI copolymers were prepared by oxidative copolymerization of OAPS and aniline, as shown in Scheme 5.1. The feed molar ratios of OAPS to aniline were 1.0/99.0 and 4.0/96.0. For clarity, the values of the POSS feed concentrations are specified in sample names. Since POSS cage is stable under acidic conditions but may undergo hydrolysis when pH value is higher than 10, to prevent the breakage of the POSS cage, an organic base, triethylamine, was used to treat the polymerization products to obtain POSS-PANI-EB. The base was then washed out using chloroform under anhydrous conditions.

Scheme 5.1 Oxidative copolymerization of OAPS and aniline to form POSS-PANI-ES, followed by conversion to POSS-PANI-EB.

The chemical structures of the PANI-EB homopolymer and POSS-PANI-EB copolymers are characterized using FTIR and elemental analysis. In order to clearly identify the structural differences between the PANI-EB and POSS-PANI-EB, 4%POSS-PANI-EB is used to elucidate the chemical structure of POSS-PANI-EB. Comparing the FTIR spectra of OAPS (Fig. 5.1a) with PANI (Fig. 5.1b), 1%POSS-PANI (Fig. 5.1c), and 4%POSS-PANI (Fig. 5.1d), it is obvious that most of the strong characteristic peaks in POSS-PANI-EB are from PANI rather than from OAPS itself and these characteristic

bands observed are associated with EB form of PANI [147, 148]. In the FTIR spectrum of 4%POSS-PANI, the band at 1594 cm^{-1} is attributable to C=C bonds of quinoid units and the band at 1504 cm^{-1} to C-C bonds of benzenoid units. The presence of the quinoid rings is also confirmed by the weak band at 1166 cm^{-1} , which is related to the electronic-like absorption of N=Q=N vibration. The band corresponding to C-H out-of-plane bending of the 1,4-disubstituted aromatic ring appears at 829 cm^{-1} , which is the evidence for the formation of poly(*p*-aniline). Comparing the FTIR spectra of the 4%POSS-PANI-EB and the linear PANI-EB, there is a strong, broad absorption band at 1112 cm^{-1} and a moderately strong band at 931 cm^{-1} only seen in the former. Both bands can be attributed to the stretching vibration of Si-O-Si. In view that the unreacted OAPS is soluble in the acidic solution and would not precipitate out to form a part of the product, the appearance of Si-O-Si stretching band indicates that PANI-EB chains have been successfully tethered onto the POSS cage, which is also supported by the elemental analysis data from 4%POSS-PANI found (Table 5.2). Although the samples have been washed 3 times using triethylamine, some Cl^- ions still doped the PANI in PANI and 4%POSS-PANI. This is the reason why the found values are less than the calculated values. The FTIR spectrum of 1%POSS-PANI-EB is similar to that of 4%POSS-PANI-EB although the bands corresponding to Si-O-Si stretching are weaker. Due to its low Si content, elemental analysis was not conducted on 1%POSS-PANI-EB.

Figure 5.1 FTIR spectra of (a) OAPS, (b) PANI-EB, (c) 1%POSS-PANI-EB and (d) 4%POSS-PANI-EB.

Table 5.2 Elemental analysis data for PANI-EB and 4%POSS-PANI-EB.

		C (%)	H (%)	N (%)	Si (%)
PANI-EB	Found	72.8	4.9	13.3	0
	Calcd.	79.5	5.0	15.5	0
4%POSS-PANI-EB	Found	59.1	4.3	10.5	6.0
	Calcd. ^a	69.4	4.6	13.5	6.8

^a The feed molar ratio of OAPS to aniline of 4/96 was used to calculate the elemental weight percentage.

5.3.2 LbL assembly of multilayer thin film

As the solubility of 4%POSS-PANI in DMAc is very low, only PANI-EB and 1%POSS-PANI-EB were used to fabricate the multilayer films. The time-dependent adsorption behavior of PANI/PAMPS and 1%POSS-PANI/PAMPS shows that the spontaneous adsorption of polyaniline occurs very rapidly. The time to reach complete adsorption takes about 15 minutes. So the dipping time for polycation and polyanion is fixed at 15 minutes. According to the time-dependent adsorption behavior of the PANI/PAMPS and 1%POSS-PANI/PAMPS adsorbed onto glass substrates (Fig. 5.2), the dipping time in polycation and polyanion solution is optimized at 15 min.

Figure 5.2 Plots of absorbance of PANI/PAMPS and 1%POSS-PANI/PAMPS multilayer films (5 bilayers) adsorbed on glass substrates as a function of dipping time.

Fig. 5.3 shows that the LbL growth of both PANI/PAMPS and 1%POSS-PANI/PAMPS multilayer thin films are linear with the thickness of each bilayer being about 2.0 nm. The other LbL assembled star-like polymer system recently published by Hammond's research group also shows the similar growth characteristics [149].

Figure 5.3 Growth curves for LbL assembled PANI/PAMPS and 1%POSS-PANI/PAMPS thin films on glass.

A characteristic peak of Si 2p is visible in Fig. 5.4a. In order to confirm that the peak is from POSS rather than from the substrate, the XPS spectrum of the silicon wafer (Fig. 5.4b) has also been measured. There are two Si 2p peaks in the XPS spectrum of the silicon wafer; the strong, sharp one originates from Si and the other from Si-O. In the XPS spectrum of (1%POSS-PANI/PAMPS)_{15.5}, the peak from Si is not observed, which indicates that surface of the wafer is completely covered by the polymers. The Si 2p peak observed thus must be from POSS in the multilayer film, which verifies that 1%POSS-PANI copolymer has been successfully incorporated into the multilayer film.

Figure 5.4 Si 2p XPS spectra of (a) (1%POSS-PANI/PAMPS)₁₅ on silicon wafer and (b) silicon wafer.

5.3.3 Surface morphology

The surface roughness of the multilayer films with the electrochromic layer on top was examined using AFM. Compared with the multilayer thin film made of linear PANI (Fig. 5.5a) and PAMPS, it is obvious that the surface roughness of 1%POSS-PANI/PAMPS multilayer thin film is higher (Fig. 5.5b). This indicates that the star-like structure of POSS-PANI can provide larger interaction area between PANI and PAMPS layers. The surface morphologies of the multilayer films with the electrochromic layer on top were also examined using FESEM. In Fig. 5.6a, we can see relatively densely packed small islands (bright regions). In contrast, in Fig. 5.6b, it is obvious that the islands are surrounded by dark regions of tens of nanometers wide, which again suggests an interdigitated morphology for 1%POSS-PANI/PAMPS multilayer film.

Figure 5.5 Tapping mode AFM images of (a) (PANI/PAMPS)_{15.5} with PANI on top and (b) (1%POSS-PANI/PAMPS)_{15.5} with 1%POSS-PANI on top.

Figure 5.6 FESEM images of (a) (PANI/PAMPS)_{15.5} with PANI on top and (b) (1%POSS-PANI/PAMPS)_{15.5} with 1%POSS-PANI on top.

5.3.4 CV studies

Based on the growth curve presented in Fig. 5.3, 50 bilayers of PANI/PAMPS and 1%POSS-PANI/PAMPS are assembled on ITO-coated glasses. The two thin films have the same thickness of 100 nm, which allows a fair comparison of the electrochromic properties. The two thin films are named as (PANI/PAMPS)₅₀ and (1%POSS-PANI/PAMPS)₅₀, respectively. The CV curves of both (PANI/PAMPS)₅₀ (Fig. 5.7a) and

(1%POSS–PANI/PAMPS)₅₀ (Fig. 5.7b) show two oxidation and reduction peaks. The first oxidation peak at lower potentials can be assigned to the leucoemeraldine to emeraldine transition, and the second oxidation peak at higher potentials is due to the transition from the emeraldine to pernigraniline state [58, 150]. Despite the similarity in the oxidation process, the reduction (dedoping) peaks of POSS–PANI, especially the ones at higher potentials corresponding to the transition from the pernigraniline to emeraldine state, are much more distinctive than those of PANI, which implies the dedoping process in the (1%POSS–PANI/PAMPS)₅₀ multilayer thin film benefits from the structure of POSS-PANI. When the anodic and cathodic peak current densities for the peaks at higher potentials are plotted against the scan rate, ν (Fig. 5.7c), approximate linear relationships are obtained for (1%POSS–PANI/PAMPS)₅₀, while for (PANI/PAMPS)₅₀ the cathodic current density shows an approximate linear relationship with the square root of the scan rate, $\nu^{1/2}$ (Fig. 5.7d), instead. This signifies that the reduction process in (PANI/PAMPS)₅₀ is largely diffusion controlled [152, 153], while the redox reactions in (1%POSS–PANI/PAMPS)₅₀ are close to non-diffusion-controlled processes in the studied scan rate range.

Figure 5.7 CV curves of (a) (PANI/PAMPS)₅₀ and (b) (1.0%POSS-PANI/PAMPS)₅₀ measured in a 0.1M LiClO₄/acetonitrile solution with scan rate of 10, 25, 50, 75 and 100 mV/s, respectively, using silver wire as the reference electrode. (c) plots of peak current densities vs. scan rate. (d) plots of peak current densities vs. square root of scan rate.

It is important to note that the redox behaviors of the spin-coated films of POSS-PANI/polymeric acid complexes are very different from that of the LbL-assembled POSS-PANI/PAMPS multilayer film [152]. Given the same film thickness (~100 nm) and testing conditions, the reduction peaks at higher potentials are indistinctive in the CV curves of the spin-coated film of 1%POSS-PANI doped with PSS (Fig. 5.8), especially at high scan rates. The key difference between the spin-coated and LbL-assembled systems is probably the conformation of the polymer chains in solutions. The LbL-assembled

multilayer films were fabricated via alternatively dipping the substrate in extremely dilute aqueous solutions of POSS-PANI-EB and the polymeric dopant (PAMPS conc. = 0.4 mg/ml). In dilute solutions, the polymer molecules exhibit extended chain conformation. Thus, the polymeric dopants are able to interact with POSS-PANI effectively via electrostatic forces. The dopant molecules that are absorbed onto the thin film via van de Waals interactions are mostly washed out in the rinse steps. XPS analysis of the composition of the multilayer thin films verifies that the 1%POSS-PANI/PAMPS multilayer film indeed has a fairly low PANI/dopant molar ratio (Table 5.3). In contrast, the POSS-PANI copolymer used in the spin-coated thin film was made by in situ polymerization, which was conducted in a concentrated solution (PSS conc. = 12.7 mg/ml) [152]. Under such a condition the polymer chains have smaller radius of gyration and interactions between dopant molecules may also be possible. Thus many acid groups may be entrapped in highly coiled dopant chains or chain clusters. In order to have a greater number of active PANI units, an excess amount of dopant molecules has to be used, which fill up the space among the arms of the star-like PANI and hence slow down the ion diffusion. This explains why at high scan rates the reduction peaks at higher potentials are indistinctive for the spin-coated film. The comparison between the LbL-assembled and spin-coated POSS-PANI thin films demonstrates that the synergy between the star-like molecular architecture of POSS-PANI and LbL assembly method enables faster kinetics for ion transportation.

Figure 5.8 CV curves of a spin-coated 1%POSS-PANI/PSS film with 100 nm thickness measured in a 0.1M LiClO₄/acetonitrile solution with scan rate of 10, 25, 50, 75 and 100 mV/s, respectively, using silver wire as the reference electrode.

Table 5.3 Composition of the multilayer films obtained from XPS analysis of (1%POSS-PANI/PAMPS)₁₅.

Name	Peak BE	At%	N/S ratio	Molar ratio of PANI unit/PAMPS unit
N 1s	400.33	74.87	2.98/1.00	1.99/1
S 2p	168.27	25.13		

It is also useful to compare the anodic-cathodic peak separation as a measure of reversibility in the switching process [154]. In Fig. 5.9, at a constant scan rate of 50 mV/s, the peaks separation value for the transition from the pernigraniline to emeraldine state is 244 mV for (PANI/PAMPS)₅₀ while that for (1%POSS-PANI/PAMPS)₅₀ is 93 mV. It

indicates that the electrochemical reactions in POSS-PANI are more reversible than those in linear PANI.

Figure 5.9 The anodic-cathodic peak separation of (PANI/PAMPS)₅₀ and (1%POSS-PANI/PAMPS)₅₀.

5.3.5 Spectroelectrochemical characterization

Fig. 5.10 show series of UV-Vis absorbance spectra of (PANI/PAMPS)₅₀ and (1%POSS-PANI/PAMPS)₅₀ under various applied potentials varying from -0.4 V to $+1.0$ V vs. Fc/Fc^+ . Both PANI and 1%POSS-PANI switch between a relatively transmissive reduced state (yellowish green) and an absorbing oxidized state (blue). The maximum change in absorbance of (PANI/PAMPS)₅₀ ($\Delta A = 0.196$ at 620 nm) (Fig. 5.10a) is similar to that of (1%POSS-PANI/PAMPS)₅₀ ($\Delta A = 0.180$ at 626 nm) (Fig. 5.10b). Without applying potential, the absorption bands for PANI and 1%POSS-PANI are centered at about 724 nm and 729 nm, respectively, with almost equal intensity (Fig. 5.10c), which implies that the content of the active units in 1%POSS-PANI is nearly the same as that in PANI. The optical properties of the thin films at different states are

fairly uniform in large areas, as demonstrated by the uniform color of the thin films (Fig. 5.10d).

Figure 5.10 Visible spectra of (a) (PANI/PAMPS)₅₀ and (b) (1%POSS-PANI/PAMPS)₅₀ under different potentials (−0.4, −0.1, +0.1, +0.2, +0.4, +0.6, +0.8, +1.0 V). (c) UV-Vis-NIR spectra of (PANI/PAMPS)₅₀ and (1%POSS-PANI/PAMPS)₅₀. (d) A photograph of (1%POSS-PANI/PAMPS)₅₀.

5.3.6 Electrochromic switching studies

The optical switching behaviors of the multilayer films are examined at λ_{max} using an UV-Vis spectrophotometer with the applied potential stepped between −0.4 V and +0.9 V at 40 s per cycle. It is striking to see that the contrast of POSS-PANI ($\Delta A = 0.203$) is significantly higher than that of PANI ($\Delta A = 0.154$) (Fig. 5.11). To understand why the

contrast of (PANI/PAMPS)₅₀ is approximately the same as that of (1%POSS-PANI/PAMPS)₅₀ in steady-state measurements while they are very different under the dynamic switching condition, it is necessary to compare Fig. 5.10a and Fig 5.10b with Fig. 5.11. The absorbance maximum of PANI measured using the chronoamperometric method ($A = 0.309$) is almost equal to that measured under the dynamic condition ($A = 0.303$) while the absorbance minimum of PANI ($A = 0.149$) on the dynamic switching curve is significantly higher than that measured using the chronoamperometric method ($A = 0.113$), which causes the relatively low contrast of PANI under the dynamic switching condition. Since the reduction process in (PANI/PAMPS)₅₀ is diffusion controlled, as shown in Fig. 5.7, obviously during chronoamperometric measurements there is enough time for the doping ions to diffuse out of the (PANI/PAMPS)₅₀ so that the reduction process can finish completely, while under the dynamic condition with cycle time fixed at 40 s, there is no enough time for the doping ions to move out of the (PANI/PAMPS)₅₀ multilayer film. Thus, the reduction process in (PANI/PAMPS)₅₀ cannot finish, which leads to the decrease in contrast of (PANI/PAMPS)₅₀. For POSS-PANI, ΔA using the chronoamperometric method is approximately the same as that obtained from the dynamic switching curve due to the faster ion transportation in (1%POSS-PANI/PAMPS)₅₀ compared with that in (PANI/PAMPS)₅₀. The relatively high contrast achieved with the 1%POSS-PANI/PAMPS multilayer thin film of only 100 nm thickness can hence be attributed to the unique morphology brought by the synergistic combination of the LbL assembly method with the star-like molecular architecture of POSS-PANI, which allows facile ion motion during the redox switching.

In addition to the improved contrast, the coloration time of the multilayer film is shortened from 6.3 seconds for (PANI/PAMPS)₅₀ to 4.0 seconds for (1%POSS-PANI/PAMPS)₅₀. This is also an enormous improvement over that of the spin-coated thin film of the same thickness made of in situ polymerized POSS-PANI/polymeric acid

complex (Fig. 5.12). It again shows the synergy between the unique material system and the LbL assembly method.

Figure 5.11 Optical switching of $(\text{PANI/PAMPS})_{50}$ and $(1\%\text{POSS-PANI/PAMPS})_{50}$ with 100 nm thickness.

Figure 5.12 Optical switching of 1%POSS-PANI/PSS film with 100 nm thickness.

When the number of 1%POSS-PANI/PAMPS bilayers is increased from 50 to 99, the thickness of the POSS-PANI multilayer films is increased from 100 to 200 nm. The optical contrast of (1%POSS-PANI/PAMPS)₉₉ is about 0.4, as shown in Fig. 5.13, which is about twice of that of (1%POSS-PANI/PAMPS)₅₀. This demonstrated the potential of the LbL assembled POSS-PANI/PAMPS thin films for enhancing the performance of electrochromic devices.

Figure 5.13 Optical switching of (1%POSS-PANI/PAMPS)₅₀ and (1%POSS-PANI/PAMPS)₉₉.

5.4 Conclusions

In summary, POSS-PANI-EB copolymers have been readily synthesized and their chemical structures verified by FTIR and elemental analysis. 1%POSS-PANI/PAMPS multilayer thin films have been successfully fabricated via LbL assembly technique. CV studies show that both the oxidation and reduction processes in the (1%POSS-PANI/PAMPS)₅₀ multilayer thin film are close to non-diffusion-controlled processes in the studied scan-rate range. Under the dynamic switching condition, the electrochromic

contrast of (1%POSS-PANI/PAMPS)₅₀ is increased by more than 30% over that of (PANI/PAMPS)₅₀ and the coloration time of (1%POSS-PANI/PAMPS)₅₀ is also significantly shorter than that of (PANI/PAMPS)₅₀. The switching kinetics of the POSS-PANI/PAMPS multilayer films is also much faster than that of spin-coated thin films of POSS-PANI/polymeric acid complexes. The improvements can be attributed to the unique morphology brought by the synergistic combination of the star-like structure of POSS-PANI and the LbL assembly method.

6. HIGH-CONTRAST ELECTROCHROMIC THIN FILMS VIA LBL ASSEMBLY OF STAR-LIKE AND SULFONATED POLYANILINE

6.1 Introduction

In Chapter 5, it has been demonstrated that the synergistic combination of the star-like structure of POSS-PANI and the LbL assembly method could greatly facilitate the electrochromic switching and improve the contrast of the electrochromic multilayer films under dynamic switching conditions. In all the studies described above, the electrochromic multilayer films are, however, composed of alternating layers of conjugated-polymer and polymeric dopant/electrolyte; the latter is electrically inactive in nature and hence cannot be redox-switched to contribute to the electrochromic contrast. To further enhance the electrochromic contrast of the multilayer thin films, a plausible approach is to fabricate fully conjugated polymeric multilayer films, in which both polycation and polyanion layers exhibit electrochromic activity. So far, only a cathodically-colored polymer pair, PXV/PEDOT:PSS [115], has been attempted. A good candidate for anodically-colored polymer pairs is PANI/highly sulfonated PANI (self-doped PANI, SPANI) as both polymers show promising electrochromic characteristics. PANI is the most widely used anodically coloring electrochromic polymer due to its ease of synthesis and good environmental stability [46, 142], and the absorption band of SPANI overlaps well with the emeraldine salt form of PANI [155, 156].

A few groups [157-159] have previously reported LbL-assembled PANI/SPANI multilayer films for sensor applications. They demonstrated that such multilayer films are stable and reversibly electroactive in electrolyte solutions [157]. However, the redox

process within the PANI/SPANI multilayer film is mainly diffusion-controlled and the highly ionically cross-linked nature of these multilayer films can be fairly compact [157], which is not ideal for fast dynamic switching of electrochromic devices. Furthermore, the motivation to use highly sulfonated PANI is to increase the content of active units in the multilayer film, which is based on the assumption that some sulfonic acid groups on SPANI chains are able to dope PANI chains to increase the reversible redox capability of PANI without disturbing the conjugated structure of SPANI. To date, no direct experimental evidence for such interchain doping has been reported and it is not clear how such interchain interactions would affect electrochromic properties of multilayer films. In this chapter, to improve the switching kinetics, the fabrication of multilayer films based on a star-like POSS-PANI polycation is shown, which can induce loose packing structure, paired with highly sulfonated SPANI. The structure and morphology of POSS-PANI/SPANI films is correlated to their electrochemical properties and electrochromic behaviors under both constant applied potentials and dynamic switching conditions. In addition, XPS and UV-Vis-NIR spectroscopy were used to probe the doping states of the aniline unit in SPANI and POSS-PANI/SPANI multilayer films, and the interaction between the two components in the multilayer films.

6.2 Experimental Section

6.2.1 Materials

SPANI (aqueous 5wt. % solution, degree of sulfonation ~100%, $M_n = 10\ 000$), [BMIM]PF₆ and PEDOT:PSS (1.3 wt% dispersion in H₂O) were purchased from Aldrich. POSS-PANI-EB was prepared by OAPS (1.0 mol.%) and aniline (99.0 mol.%) using the same method reported in Chapter 5. PVDF-HFP (solef[®]11008) was purchased from Solvay Solexis. Super-critical carbon dioxide (SCCO₂) treated electrospun PVDF

membranes were prepared according to the reported method [160]. Other chemicals are the same as reported in Chapter 4.

6.2.2 Preparation of dipping solutions

The preparation method for POSS-PANI (polycation) and PAMPS (polyanion) solutions is the same as reported in Chapter 4. SPANI (polyanion) solution (0.78 mM) was prepared by dissolving SPANI in water under stirring and the pH value of the SPANI aqueous solution was adjusted to 2.5.

6.2.3 LbL assembly of multilayer thin films

Multilayer thin films were constructed using a HMS 70 slide stainer. The procedure for substrate treatment and the LbL assembly of the multilayer thin films were the same as reported in Chapter 4 except that the dipping time in SPANI solution was 5 min. 15 bilayers of POSS-PANI/SPANI ((POSS-PANI/SPANI)₁₅) with SPANI on top and 15.5 bilayers of POSS-PANI/SPANI ((POSS-PANI/SPANI)_{15.5}) with POSS-PANI on top are assembled on silicon wafer for XPS measurement. For the fabrication of spin-coated SPANI sample, the original SPANI solution was diluted using Milli-Q water and stirred for 1 hour for use.

6.2.4 Thin film characterization

Thickness measurements were performed with an Alfa-step Q surface profiler. XPS experiments are the same as reported in Chapter 4. In curve fitting, all core-level spectra were deconvoluted into Gaussian component peaks, the line width (FWHM) of the Gaussian peaks was maintained constant for all components in a particular spectrum and the Shirley background was subtracted. A four-point probe system and WAXD measurements are the same as reported in Chapter 3. The electrochemical experiments are the same as reported in Chapter 4.

6.2.5 Fabrication and characterization of the complementary electrochromic device

PEDOT:PSS was spin-coated (1600 rpm, 60 s) onto cleaned ITO-glass and its thickness is about 100 nm. In the complementary electrochromic device (Fig. 6.1), the anodically colored electrochromic thin films of (POSS-PANI/SPANI)₅₀ is used as the active layer, the cathodically colored electrochromic thin film of PEDOT:PSS is used as the ion storage and the ionic liquid of [BMIM]PF₆ hosted in electrospun PVDF-HFP membrane is used as the electrolyte layer. The thickness of PVDF membrane is about 33 μm. Complementary electrochromic device with a sandwich structure of ITO-glass|(POSS-PANI/SPANI)₅₀[[BMIM]PF₆-PVDF(HFP)]PEDOT:PSS|ITO-glass were then fabricated. The spectroelectrochemical properties of the device were characterized using the same methods as reported in Chapter 3.

Figure 6.1 Configuration of the complementary electrochromic device of ITO-glass|(POSS-PANI/SPANI)₅₀[[BMIM]PF₆-PVDF(HFP)]PEDOT:PSS|ITO-glass.

6.3 Results and discussion

6.3.1 Interactions between POSS-PANI and SPANI

LbL assembly process can create macromolecular complexes by alternating exposure of an ionized substrate to dilute aqueous solutions or dispersions of materials with opposite attractive affinities [114, 115]. The LbL assembly scheme for this work is shown in Fig. 6.2a. In order to make a fair comparison between POSS-PANI/SPANI and POSS-PANI/PAMPS, the dipping time and concentration of SPANI polyanion solution are controlled to ensure that the thickness of each bilayer is about 2.0 nm, similar to that of POSS-PANI/PAMPS. Fig. 6.2b shows that the LbL growth of POSS-PANI/SPANI multilayer films as a function of bilayer number is linear under the conditions used. The thickness of (POSS-PANI/SPANI)₅₀, (POSS-PANI/PAMPS)₅₀, and spin-coated SPANI are all controlled to be 100 nm.

Figure 6.2 (a) A scheme showing the structure of POSS-PANI/SPANI multilayer films, (b) the growth curve for LbL assembly of POSS-PANI/SPANI multilayer films on glass.

For the system under study, electrostatic interaction between the sulfonic acid groups attached to the backbone of SPANI and the cationic amine nitrogen groups in POSS-

PANI provide the driving force for the LbL assembly. To study the interaction between POSS-PANI and SPANI, XPS is used to probe the different states of nitrogen and to determine the proportion of these species to the total amount of nitrogen atoms [161-166]. In order to differentiate the different states of cationic nitrogen, N 1s peak was analyzed using peak fitting method. The XPS spectra and the fitting curves for N 1s peaks are given in Fig. 6.3. The data obtained from curve fitting are summarized in Table 6.1.

Figure 6.3 XPS N 1s of (a) spin-coated SPANI, (b) (POSS-PANI/SPANI)₁₅ and (c) (POSS-PANI/SPANI)_{15.5}.

Table 6.1 N 1s data of various samples obtained from XPS analysis.

Peak and proportion		Spin-coated SPANI	(POSS- PANI/SPANI) ₁₅	(POSS- PANI/SPANI) _{15.5}
N1s binding energy (eV)	$\begin{array}{c} \text{H} \\ \\ -\text{N}- \\ \\ \bullet+ \end{array}$	399.6	399.9	399.8
	$\begin{array}{c} \text{H} \\ \\ -\text{N}- \\ \\ \bullet+ \end{array}$ and $\begin{array}{c} \text{H} \\ \\ -\text{N}= \\ \\ + \end{array}$	401.1	400.9	400.9
	$\begin{array}{c} \text{H} \\ \\ -\text{N}^+- \\ \\ \text{H} \end{array}$	402.1	402.2	402.2
N1s proportion (%) ^a	$\begin{array}{c} \text{H} \\ \\ -\text{N}- \\ \\ \bullet+ \end{array}$	40.6	58.9	59.6
	$\begin{array}{c} \text{H} \\ \\ -\text{N}- \\ \\ \bullet+ \end{array}$ and $\begin{array}{c} \text{H} \\ \\ -\text{N}= \\ \\ + \end{array}$	19.4 ^b	28.3	30.5
	$\begin{array}{c} \text{H} \\ \\ -\text{N}^+- \\ \\ \text{H} \end{array}$	40.0	12.8	9.9

^a The values were determined via the curve-fitting of N 1s core-level spectra of spin-coated SPANI of 30-nm thickness, (POSS-PANI/SPANI)₁₅ and (POSS-PANI/SPANI)_{15.5}.

^b For spin-coated SPANI, the value is determined from the cationic nitrogen atoms at polaron state.

In the XPS fitting curves, the peaks at about 400 eV are due to the undoped amine units. The peaks at about 401 eV are associated with cationic nitrogen atoms at polaron and bipolaron states, while the peaks at about 402 eV are correlated to sp³ protonated amine units. The latter occurs at a higher BE because of the stronger electron localization associated with poorer conjugation [163, 167]. When one layer of POSS-PANI is deposited onto the multilayer film of 15 bilayers ((POSS-PANI/SPANI)₁₅), the proportion of polaron and bipolaron cationic nitrogen increases from 28.3% for (POSS-PANI/SPANI)₁₅ to 30.5% for (POSS-PANI/SPANI)_{15.5}, while the proportion of high-

binding-energy protonated amine decreases from 12.8% for (POSS-PANI/SPANI)₁₅ to 9.9% for (POSS-PANI/SPANI)_{15.5}. The chemical composition of the probed surface for (POSS-PANI/SPANI)₁₅ and (POSS-PANI/SPANI)_{15.5} is characterized according to the XPS analysis from the corrected N 1s and S 2p core-level spectral area ratio (Fig. 6.4). The ratio of S/N from the probed surface of (POSS-PANI/SPANI)₁₅ is equal to 22.2/77.8 while the ratio of S/N from the probed surface of (POSS-PANI/SPANI)_{15.5} is equal to 21.9/78.1, indicating that the chemical composition of the two surfaces is almost the same. Thus, the increase of the proportion of the polaron and bipolaron cationic nitrogen and the decrease of the proportion of the high-binding-energy protonated amine indicated that the observed difference is due to the change in ionic bonding. We attribute this difference to the reorganization of SPANI chains to effectively dope POSS-PANI to form more polarons and bipolarons, which is accompanied by a decrease in the amount of protonated amine units in SPANI layers. Since the protonated amine units interfere with the formation of polarons and bipolarons to interrupt the order of the polaron lattice [168, 169], the decrease in the amount of protonated amine units extends the conjugated π system in POSS-PANI/SPANI thin film and facilitates redox switching.

Figure 6.4 Plots of the corrected N 1s and S 2p core-level spectra for (a) (POSS-PANI/SPANI)₁₅ and (b) (POSS-PANI/SPANI)_{15.5}.

The extension of conjugation also influences band gap energies and electrical conductivity values of the polymer films. UV-Vis-NIR spectra of the spin-coated SPANI, (POSS-PANI/PAMPS)₅₀, and (POSS-PANI/SPANI)₅₀ are shown in Fig. 6.5a. The peaks at about 800 nm for (POSS-PANI/PAMPS)₅₀ and (POSS-PANI/SPANI)₅₀ are due to the trapped excitons centered on quinoid moieties [170], which do not appear in the spectrum of the spin-coated SPANI. The peak at about 430 nm for (POSS-PANI/PAMPS)₅₀ and at 475 nm for the spin-coated SPANI are due to polaron absorption [170-172]. When the polaron absorption peaks are enlarged (Fig. 6.5b), two weak polaron peaks can be observed from the spectrum of (POSS-PANI/SPANI)₅₀. By comparing these two peaks with the polaron peaks of the spin-coated SPANI and (POSS-PANI/PAMPS)₅₀, one polaron peak for (POSS-PANI/SPANI)₅₀ can be assigned to POSS-PANI while the other to SPANI component. In order to calculate band gap energies, plots of $(\alpha h\nu)^2$ versus $h\nu$ [46, 173-175] are obtained for the spin-coated SPANI, (POSS-PANI/PAMPS)₅₀ and (POSS-PANI/SPANI)₅₀. The optical band gap energy of the conjugated polymers can be obtained using the equations below (Eq. 6.1):

$$\begin{aligned} \alpha h\nu &= B(h\nu - E_g)^m \\ \alpha &= \frac{1}{t} \ln\left(\frac{1}{T}\right) \end{aligned} \quad (6.1)$$

In Eq. 6.1, α is the optical absorption coefficient, B is an energy-independent constant, $h\nu$ is the photon energy, E_g is the optical band gap, index m is a parameter related to the type of optical transitions (for PANI, $m = 1/2$), t is the thickness of the film and T is the transmittance. $(\alpha h\nu)^2$, which is obtained from the UV-Vis absorption curves, was plotted as a function of photon energy ($h\nu$) (Fig. 6.5c) to determine the band gaps. By extrapolating the linear portion of the plots to $(\alpha h\nu)^2 = 0$, the optical band gap energies were obtained. The band gap of POSS-PANI decreases from 2.60 eV in (POSS-

PANI/PAMPS)₅₀ to 2.48 eV in (POSS-PANI/SPANI)₅₀ and the band gap of SPANI decreases from 2.47 eV in the spin-coated SPANI to 2.36 eV in (POSS-PANI/SPANI)₅₀.

Figure 6.5 (a) UV-Vis-NIR spectra of the spin-coated SPANI, (POSS-PANI/PAMPS)₅₀ and (POSS-PANI/SPANI)₅₀, (b) polaron absorption of the spin-coated SPANI, (POSS-PANI/PAMPS)₅₀ and (POSS-PANI/SPANI)₅₀, and (c) plot of $(\alpha h\nu)^2$ vs. $h\nu$ for spin-coated SPANI, (POSS-PANI/PAMPS)₅₀ and (POSS-PANI/SPANI)₅₀.

In addition, the electrical conductivity of (POSS-PANI/SPANI)₅₀ is an order of magnitude higher than those of spin-coated SPANI and (POSS-PANI/PAMPS)₅₀ films (Table 6.2). WAXD results (Fig. 6.6) show that all three thin films are dominantly amorphous and their differences in electrical conductivity values are not due to their

difference in degree of crystallinity or crystal size. The lower band gap and higher electrical conductivity of (POSS-PANI/SPANI)₅₀ thus confirm the strong interaction between POSS-PANI and SPANI which extends the conjugation in POSS-PANI/SPANI films and may significantly influence electrochromic properties of (POSS-PANI/SPANI)₅₀.

Figure 6.6 X-ray diffraction patterns of spin-coated SPANI, (POSS-PANI/PAMPS)₅₀ and (POSS-PANI/SPANI)₅₀. The X-ray diffraction measurements of the thin films were performed using a Shimadzu 6000 X-ray diffractometer with CuK radiation at scan rate of 0.2°/min.

Table 6.2 Band gap and electrical conductivity.

Materials	Band gap (eV)	Electrical conductivity (S/cm)
Spin-coated SPANI	2.47	4.65×10^{-3}
(POSS-PANI/SPANI) ₅₀	2.36, 2.48	1.15×10^{-2}
(POSS-PANI/PAMPS) ₅₀	2.60	2.55×10^{-3}

6.3.2 CV studies

According to the growth curve shown in Fig. 6.2b, 50 bilayers of POSS-PANI/SPANI was assembled on ITO-coated glass with the overall thickness of about 100 nm. SPANI was also spin-coated on ITO-coated glass and the thickness was controlled at about 100 nm in order to make a fair comparison between SPANI and POSS-PANI/SPANI. The oxidation and reduction peaks in CV curves of (POSS-PANI/SPANI)₅₀ (Fig. 6.7a) are more distinct than those of the spin-coated SPANI (Fig. 6.7b), which implies that the redox process in the (POSS-PANI/SPANI)₅₀ multilayer thin film is faster than that in spin-coated SPANI. Comparing the CV curves (Fig. 6.7c) of the spin-coated SPANI and (POSS-PANI/SPANI)₅₀, as well as that of (POSS-PANI/PAMPS)₅₀, the transition between the emeraldine and pernigraniline state is shifted to lower potentials for (POSS-PANI/SPANI)₅₀ compared with those of (POSS-PANI/PAMPS)₅₀, indicating a more favorable electrochemical reaction. The strong interaction between POSS-PANI and SPANI layers results in shifting of oxidation and reduction potentials to lower values, making this system more accessible. When the anodic and cathodic peak current densities for the peaks at higher potentials are plotted against the scan rate, ν (Fig. 6.7d), approximate linear relationships are obtained for (1%POSS-PANI/SPANI)₅₀, while for the spin-coated SPANI the anodic and cathodic current densities shows an approximate linear relationship with the square root of the scan rate, $\nu^{1/2}$ (Fig. 6.7e), instead. This signifies that the redox process in the spin-coated SPANI is largely diffusion controlled [152, 153], while the redox reactions in (POSS-PANI/SPANI)₅₀ are not diffusion-controlled processes in the studied scan rate range, which is similar to the redox process of (POSS-PANI/PAMPS)₅₀ reported in Chapter 5.

Figure 6.7 CV curves of (a) (POSS-PANI/SPANI)₅₀ and (b) spin-coated SPANI measured in a 0.1M LiClO₄/acetonitrile solution with scan rate of 10, 25, 50, 75 and 100 mV/s, respectively, using silver wire as the reference electrode. (c) CV curves of (POSS-PANI/PAMPS)₅₀ (blue line), spin-coated SPANI (black line) and (POSS-PANI/SPANI)₅₀ (red line) measured in a 0.1 M LiClO₄/acetonitrile solution with scan rate of 25 mV/s. (d) plots of peak current densities vs. scan rate and (e) plots of peak current densities vs. square root of scan rate.

6.3.3 Spectroelectrochemical characterization

Fig. 6.8 shows two series of UV-Vis absorbance spectra of (POSS-PANI/SPANI)₅₀ and

the spin-coated SPANI under various applied potentials varying from -0.4 V to $+0.8$ V vs. Fc/Fc^+ . Both the spin-coated SPANI and $(\text{POSS-PANI/SPANI})_{50}$ can be switched between a relatively transmissive reduced state (yellowish green) and an absorbing oxidized state (blue). The maximum change in absorbance of $(\text{POSS-PANI/SPANI})_{50}$ ($\Delta A = 0.25$ at 592 nm) (Fig. 6.8a) is the same as that of the spin-coated SPANI ($\Delta A = 0.25$ at 630 nm) (Fig. 6.8b). Comparing the absorbance curves under $+0.8$ V and -0.4 V for $(\text{POSS-PANI/SPANI})_{50}$ with those of $(\text{POSS-PANI/PAMPS})_{50}$ (Fig. 6.8c), the maximum contrast of $(\text{POSS-PANI/SPANI})_{50}$ is much higher than that of $(\text{POSS-PANI/PAMPS})_{50}$ as both components in $(\text{POSS-PANI/SPANI})_{50}$ can contribute to the electrochromic contrast. The λ_{max} for $(\text{POSS-PANI/SPANI})_{50}$ is shifted to a slightly lower wavelength in comparison with that of $(\text{POSS-PANI/PAMPS})_{50}$, suggesting that $(\text{POSS-PANI/SPANI})_{50}$ multilayer film can be more easily oxidized. This is consistent with the CV observation that the oxidation peak potential for the $(\text{POSS-PANI/SPANI})_{50}$ multilayer film is lower than that of $(\text{POSS-PANI/PAMPS})_{50}$.

Figure 6.8 Visible spectra of (a) (POSS-PANI/SPANI)₅₀, (b) spin-coated SPANI under different potentials (−0.4, −0.1, +0.1, +0.2, +0.4, +0.6, +0.8 V) and (c) the absorbance curves under +0.8 V (solid lines) and −0.4 V (dash lines) for (POSS-PANI/SPANI)₅₀ (red line), (POSS-PANI/PAMPS)₅₀ (blue line) and spin-coated SPANI (black line).

6.3.4 Electrochromic switching studies

The optical switching behaviors of the multilayer films are examined at λ_{max} using an UV-Vis-NIR spectrophotometer with the applied potential stepped between −0.4 V and +0.8 V at 60 s per cycle. It is striking to see that the contrast of (POSS-PANI/SPANI)₅₀ ($\Delta A = 0.26$) is significantly higher than those of both (POSS-PANI/PAMPS)₅₀ ($\Delta A = 0.19$) and the spin-coated SPANI ($\Delta A = 0.15$) under such a dynamic switching

condition (Fig. 6.9). To understand why the contrast of the spin-coated SPANI is approximately the same as that of (POSS-PANI/SPANI)₅₀ under constant applied potentials while it is much lower under the dynamic switching condition, it is necessary to compare Fig. 6.8c with Fig. 6.9. The comparison data are listed in Table 6.3. The absorbance maximum of the spin-coated SPANI measured under the dynamic condition ($A = 0.26$) is lower than that measured using the chronoamperometric method ($A = 0.30$) and the absorbance minimum of SPANI measured under dynamic condition ($A = 0.11$) is higher than that measured using the chronoamperometric method ($A = 0.05$), indicating that a significant part of SPANI units is not accessible under the dynamic switching condition, and therefore cannot be switched. Since the redox process in the spin-coated SPANI is diffusion controlled, there is enough time during chronoamperometric measurements for the doping ions to diffuse in and out of the SPANI film so that the redox process can be fully completed. However, under a dynamic switching condition of 60 seconds, there is not enough time for the doping ions to move in and out of spin-coated SPANI film. Thus, during the dynamic switching, the redox process in the spin-coated SPANI film cannot finish completely in 60 seconds, which leads to the lower contrast of the spin-coated SPANI under the dynamic switching condition. The contrast values of (POSS-PANI/SPANI)₅₀ and (POSS-PANI/PAMPS)₅₀ are almost unchanged whether the measurement method is chronoamperometric or dynamic switching, indicating that all PANI units are easily accessible and can be switched within 60 seconds. Thus, the significantly higher contrast achieved with POSS-PANI/SPANI can be attributed to the greater amount of active units induced by interchain interaction between POSS-PANI and SPANI, the loosely packed structure of POSS-PANI brought by its star-like molecular architecture, and the unique morphology created by the LbL assembly that facilitates the ion transport during the redox reactions.

Figure 6.9 Optical switching of $(\text{POSS-PANI/SPANI})_{50}$, $(\text{POSS-PANI/PAMPS})_{50}$ and spin-coated SPANI with 100 nm thickness.

Table 6.3 Electrochromic properties of all samples.

Materials	ABS λ_{max} (nm)	Contrast measured using the chronoamperometric method	Contrast measured under the step potential
Spin-coated SPANI	630	0.25 (from 0.30 to 0.05)	0.15 (from 0.26 to 0.11)
$(\text{POSS-PANI/SPANI})_{50}$	592	0.25 (from 0.41 to 0.16)	0.26 (from 0.43 to 0.17)
$(\text{POSS-PANI/PAMPS})_{50}$	626	0.17 (from 0.30 to 0.13)	0.19 (from 0.31 to 0.12)

6.3.5 Complementary electrochromic device

6.3.5.1 Electrochromic property of PEDOT:PSS

The CV curves of spin-coated PEDOT:PSS film is shown in Fig. 6.10a. The CV shape is qualitatively similar to those of other PEDOT films published [111, 176] before. The broad reduction peak is most visible when the scan rate is 100 mV/s. Due to the chemical oxidation of reduced PEDOT by molecular oxygen, the activity of the oxidative sweep is less visible. The spectral response of spin-coated PEDOT:PSS thin film under constant applied potentials is shown in Fig. 6.10b. PEDOT:PSS could be switched between a relatively transmissive state (transparent) under an applied potential of +0.4 V and absorbing states (dark blue) under an applied potential of -0.7 V. The λ_{max} for PEDOT:PSS thin film is about 620 nm. Comparing the absorbance curves of spin-coated PEDOT:PSS under +0.4 V and -0.7 V with those of (POSS-PANI/SPANI)₅₀ under -0.4 V and +0.8 V (Fig. 6.10c), the λ_{max} of (POSS-PANI/SPANI)₅₀ is close to that of spin-coated PEDOT:PSS. Thus, the pair of anodically colored electrochromic thin films of (POSS-PANI/SPANI)₅₀ and cathodically colored electrochromic thin film of PEDOT:PSS can be used in the complementary electrochromic device.

Figure 6.10 CV curves of (a) PEDOT:PSS with 100 nm thickness measured in a 0.1 M $LiClO_4$ /acetonitrile solution with scan rate of 10, 25, 50, 75 and 100 mV/s. (b) Visible spectra of PEDOT:PSS under different potentials (+0.4, +0.2, -0.1, -0.2, -0.3, -0.4, -0.5, -0.6, -0.7 V). (c) Visible spectra of PEDOT:PSS under +0.4 V and -0.7 V and (1%POSS-PANI/SPANI)₅₀ under -0.4 V and +0.8 V.

6.3.5.2 Electrochromic properties of the device

The two-electrode CV curve of the complementary electrochromic device with scan rate of 25 mV/s is shown in Fig 6.11a, which indicated that the complementary electrochromic device can be fully switched between -1.8 V and +1.8 V. The device is operated by simultaneous oxidation of one electrochromic layer and reduction of the other.

Fig. 6.11b shows a series of UV-Vis absorbance spectra of the complementary electrochromic device under constant applied potentials varying from -1.8 V to $+1.8$ V. The complementary electrochromic device can be switched between a relatively transmissive state and an absorbing state. The λ_{max} for the device is about 650 nm. The optical switching behaviors of the device were also examined at 650 nm with the potential stepped between -1.7 V and $+1.7$ V at 60 s per cycle (Fig. 6.11c). It is clear that the complementary electrochromic device can work very well under dynamic switching. The real photographs of the complementary electrochromic device at relatively transmissive state (transparent) and absorbing state (dark blue) are shown in Fig 6.12a and Fig 6.12b respectively. The above experimental results demonstrated the potential of the POSS-PANI/SPANI multilayer films for electrochromic applications. However, the limitations to this complementary electrochromic device are the unbalance of the opposite electrochemical processes in the POSS-PANI/SPANI layer and PEDOT:PSS layer because of their different charge densities and its coloration time (13 s) because of the large ions' size of ionic liquid.

Figure 6.11 (a) The CV curve of the complementary electrochromic device with scan rate of 25 mV/s. (b) Visible spectra of the device under different potentials (−1.8, −1.5, −1.0, 0, +1.0, +1.5, +1.8 V). (c) Optical switching at 650 nm for the device under square-wave potentials oscillating between −1.7 and +1.7 V.

Figure 6.12 The photographs of the complementary electrochromic device at (a) transmissive state and (b) absorbing state.

6.4 Conclusions

In summary, POSS-PANI/SPANI multilayer thin films have been successfully fabricated via LbL assembly technique. XPS analysis shows that there is strong interaction between POSS-PANI and SPANI that increases the amount of electroactive units and extends the conjugation length in POSS-PANI/SPANI. This interaction leads to lower band gap energies and higher electrical conductivity values compared with the values obtained from underlying components POSS-PANI and neat spin-cast films of SPANI. Based on the CV studies, the interaction between POSS-PANI and SPANI has also altered the electrochemical properties of POSS-PANI and SPANI components. The oxidation and reduction potentials have been shifted to lower values, resulting in a more favorable redox reaction for the LbL assembled POSS-PANI/SPANI system. Furthermore, as opposed to the spin-coated SPANI film, the redox processes in the POSS-PANI/SPANI multilayer thin film are not diffusion-controlled. Finally, the electrochromic contrast of POSS-PANI/SPANI is increased by more than 35% over that of POSS-PANI/PAMPS and the switching kinetics of the POSS-PANI/SPANI multilayer film is much faster than that of the spin-coated SPANI. These findings indicate that the LbL method can be used to actually enhance the functional properties of polymers via intimate blending with synergistic polyions. In the case demonstrated here, the combination of a star-like conjugated molecular architecture and the self-doping and ionically conductive aspects of SPANI, brought together through the use of LbL assembly, has proven effective in achieving high contrast and fast switching electrochromic polymer films. The electrochromic properties of the complementary device also demonstrated the potential of the POSS-PANI/SPANI multilayer films for electrochromic applications.

7. CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

In summary, 4.0%HACP-PANI/DBSA can achieve higher contrast compared with linear PANI because of its loose packing structure, which led to a considerable increase in ionic conductivity and, as a result, more effective doping. Therefore, the introduction of a CP core covalently bonded to electrochromic polymers at an appropriate molar percentage would offer an alternative way to generate a loosely packed structure and enhance the contrast of certain electrochromic polymers. However, the contrast and switching kinetics of 4%HACP-PANI/PAMPS is not improved compared with those of PANI/PAMPS under dynamic switching because of its densely packed structure brought by the flexible -O- linkage in HACP-PANI.

In contrast to HACP-PANI, POSS-PANI is more rigid because of the absence of the flexible O groups. The electrochromic contrast of (1%POSS-PANI/PAMPS)₅₀ is increased by more than 30% over that of (PANI/PAMPS)₅₀ and the switching kinetics of (POSS-PANI/PAMPS)₅₀ is much faster than those of (PANI/PAMPS)₅₀ and spin-coated POSS-PANI/polymeric acid complexes thin film under dynamic switching. The improvements can be attributed to the unique morphology brought by the synergistic combination of the star-like structure of POSS-PANI and the LbL assembly technique.

In order to improve the electrochromic contrast further, fully conjugated polymeric multilayer thin films of POSS-PANI/SPANI were fabricated via LbL assembly. The results show that SPANI can dope POSS-PANI effectively to form more polarons and bipolarons, which results in a decrease in the amount of protonated amine units in SPANI

layers. This interaction leads to lower band gap energies, higher electrical conductivity values and a lower oxidation and reduction potentials compared with the values obtained from PAMPS doped POSS-PANI, which results into a more favorable redox reaction for the LbL assembled POSS-PANI/SPANI system. The synergistic combination of the star-like structure of POSS-PANI, the LbL assembly technique and the use of conjugated polymers as both polycation and polyanion layers is an effective method to achieve higher contrast and faster switching kinetics under dynamic switching conditions as compared with LbL-assembled POSS-PANI/PAMPS and spin-coated SPANI respectively.

7.2 Recommendations for future research

My Ph.D work has demonstrated that the synergistic combination of the star-like structure of POSS-PANI and the LbL assembly is an effective method to achieve high contrast and faster switching kinetics under dynamic switching. I believe that this approach may be applied to other conjugated polymer systems. Some recommendations for future research are shown as follows:

(1) To investigate if there is a synergistic effect of star-like molecular architecture with LbL assembly for other conjugated polymers systems.

At present, many works in the electrochromic research field are focused on the synthesis of novel linear electrochromic monomers and their polymers, such as thiophene, pyrrole, azulene and their derivatives. The most commonly used film fabrication methods are spin-coating and electropolymerization. Modification the structure of the linear conjugated polymers by tethering them onto POSS nanocage or other star-like core, such as C_{60} , could be a reasonable and effective method to improve the electrochromic contrast and switching speed of the conventional conjugated polymers.

(2) Optimization of the components' charge densities in complementary electrochromic devices fabricated via LbL assembly.

Cycle life is one of the most important parameters for an electrochromic device. The cycle life of an electrochromic device is closely related to the amount of injected/ejected charge per unit area across electrochromic layer and ion storage layer. It is very important to adjust the injected/ejected charge per unit area across the electrochromic layer and ion storage layer to balance the opposite electrochemical processes in the two different layers. One of the advantages of LbL assembly technique is to create films of macromolecular complexes with nanometer-level control and allow the incorporation of many different functional materials into a single film at a full range of compositions. The charge per unit area in the two electrodes of the device is influenced by the thickness of the coated films and the types of the electrochromic materials because different types of electrochromic materials have different charge densities [111, 115]. Thus, LbL assembly technique provides a good approach for us to control the charge per unit area across the electrochromic layer and the ion storage layer during redox switching easily via adjusting the thickness of the electrochromic layer and the ion storage layer or using different types of electrochromic materials in complementary electrochromic devices.

(3) Preparation of novel electrolytes using ionic liquids with different salts hosted in electrospun PVDF membrane.

The ions' size in electrolyte solutions has a high effect on the switching speed and stability of the complementary device. Although ionic liquids have many advantages, the large size of their ions, especially cations, has an adverse effect for the ions' transfer in/out of the LbL assembled electrochromic films during redox switching. Thus, novel electrolyte using ionic liquid with small ionic salts (LiPF_6 , LiBF_4) hosted in electrospun PVDF membrane should be feasible method to improve the switching speed and stability

of LbL assembled complementary electrochromic devices. The electrochemical stability of ionic liquid-loaded PVDF membrane and the ionic conductivities of the ions through the LbL-assembled electrochromic films should be studied.

(4) Application of POSS-PANI/SPANI multilayer thin films in the IR range.

It has been demonstrated that SPANI can achieve high contrast in the IR range. The electrical conductivity of electrochromic materials has a significant impact on the materials' IR absorption [64, 177], while the electrical conductivity is also related to its crystallinity [178]. It has been demonstrated that the crystallinity of spin-coated SPANI and (POSS-PANI/SPANI)₅₀ is the same while the electrical conductivity of (POSS-PANI/SPANI)₅₀ is much higher than that of spin-coated SPANI. Thus, the study on the relationship between electrical conductivity and IR absorption may help us to understand the electrochromic behaviors of PANI derivatives in the IR range.

REFERENCES

1. Mortimer, R. J.; Dyer, A. L.; Reynolds, J. R. *Displays* 2006, 27, 2.
2. O'Brien, N. A.; Gordon, J.; Mathew, H.; Hichwa, B. P. *Thin Solid Films* 1999, 312.
3. Hsiao, S. H.; Liou, G. S.; Kung, Y. C.; Yen, H. J. *Macromolecules* 2008, 41, 2800.
4. Colley, R. A.; Budd, P. M.; Owen, J. R.; Balderson, S. *Polym. Int.* 2000, 49, 371.
5. Franke, E. B.; Trimble, C. L.; Schubert, M.; Woollam, J. A.; Hale, J. S. *Appl. Phys. Lett.* 2000, 77, 930.
6. Cecchet, F.; Bignozzi, C. A.; Paolucci, F.; Marcaccio, M. *Synth. Met.* 2006, 156, 27.
7. Cho, S. I.; Kwon, W. J.; Choi, S.-J.; Kim, P.; Park, S.-A.; Kim, J.; Son, S. J.; Xiao, R.; Kim, S.-H.; Lee, S. B. *Adv. Mater.* 2005, 17, 171.
8. Rye, J.-H.; Lee, J.-H.; Han, S.-J.; Suh, K.-D. *Macromol. Rapid Comm.* 2006, 27, 1156
9. Kumar, A.; Welsh, D. M.; Morvant, M. C.; Piroux, F.; Abboud, K. A.; Reynolds, J. R. *Chem. Mater.* 1998, 10, 896.
10. Welsh, D. M.; Kumar, A.; Meijer, E. W.; Reynolds, J. R. *Adv. Mater.* 1999, 11, 1379
11. Xiong, S.; Xiao, Y.; Ma, J.; Zhang, L.; Lu, X. *Macromol. Rapid Comm.* 2007, 28, 281
12. Platt, J. R. *J. Chem. Phys.* 1961, 34, 862.
13. Somani, P. R.; Radhakrishnan, S. *Mater. Chem. Phys.* 2003, 77, 117.
14. Deb, S. K. *Appl. Optics* 1969, 3, 192.
15. Rauh, R. D. *Electrochim. Acta* 1999, 44, 3165.
16. Agrawal, A.; Cronin, J. P.; Zhang, R. *Sol. Energ. Mat. Sol. C.* 1993, 9.
17. Livage, J.; Ganguli, D. *Sol. Energ. Mat. Sol. C.* 2001, 365.
18. Wang, H.; Yan, M.; Jiang, Z. *Thin Solid Films* 2001, 401, 211.

-
19. Nishio, K.; Watanabe, Y.; Tsuchiya, T. *Thin Solid Films* 1999, 350, 96.
 20. Shim, H.-S.; Shinde, V. R.; Kim, H. J.; Sung, Y.-E.; Kim, W. B. *Thin Solid Films* 2008, 516, 8573.
 21. Cordoba de Torresi, S. I.; Gorenstein, A. *Electrochim. Acta* 1992, 37, 2015.
 22. Ozkan Zayim, E.; Turhan, I.; Tepehan, F. Z.; Ozer, N. *Sol. Energy Mater. Sol. Cells* 2008, 92, 164.
 23. Macrelli, G.; Poli, E. *Electrochim. Acta* 1999, 44, 3137.
 24. Vickers, S. J.; Ward, M. D. *Electrochem. Commun.* 2005, 7, 389.
 25. Ottaviani, M.; Panero, S.; Morzilli, S.; Scrosati, B.; Lazzari, M. *Solid State Ionics* 1986, 20, 197.
 26. Dhanasankar, M.; Purushothaman, K. K.; Muralidharan, G. *Solid State Sci.* 12, 246.
 27. Moliton, A.; Hiorns, R. C. *Polym. Int.* 2004, 53, 1397.
 28. Jagur-Grodzinski, J. *Polym. Adv. Technol.* 2002, 13, 615.
 29. Yildiz, U. H.; Sahin, E.; Akhmedov, I. M.; Tanyeli, C.; Toppare, L. *J. Polym. Sci. Pol. Chem.* 2006, 44, 2215
 30. Beaujuge, P. M.; Reynolds, J. R. *Chemical Reviews* 2010, 110, 268.
 31. Gunbas, G. E.; Durmus, A.; Toppare, L. *Adv. Funct. Mater.* 2008, 18, 2026.
 32. Wang, X.; Ng, J. K. P.; Jia, P.; Lin, T.; Cho, C. M.; Xu, J.; Lu, X.; He, C. *Macromolecules* 2009, 42, 5534
 33. Wu, C. G.; Lu, M. I.; Chang, S. J.; Wei, C. S. *Adv. Funct. Mater.* 2007, 17, 1063.
 34. Sapp, S. A.; Sotzing, G. A.; Reynolds, J. R. *Chem. Mater.* 1998, 10, 2101.
 35. Schwendeman, I.; Gaupp, C. L.; Hancock, J. M.; Groenendaal, L.; Reynolds, J. R. *Adv. Funct. Mater.* 2003, 13, 541.
 36. Sonmez, G.; Meng, H.; Zhang, Q.; Wudl, F. *Adv. Funct. Mater.* 2003, 13, 726
 37. Erden, A.; Sahin, E.; Gullu, M.; Toppare, L. *Eur. Polym. J.* 2006, 42, 1866.
 38. Bulut, U.; Toppare, L.; Yilmaz, F.; Yagci, Y. *Eur. Polym. J.* 2004, 40, 2421.

-
39. Bulut, U.; Yilmaz, F.; Yagci, Y.; Toppare, L. *React. Funct. Polym.* 2004, 61, 63.
40. Pang, Y.; Xu, H.; Li, X.; Ding, H.; Cheng, Y.; Shi, G.; Jin, L. *Electrochem. Commun.* 2006, 8, 1757.
41. Camurlu, P.; Sahmetlioglu, E.; Sahin, E.; Akhmedov, I. M.; Tanyeli, C.; Toppare, L. *Thin Solid Films* 2008, 516, 4139.
42. Mudigonda, D. S. K.; Loveday, D. C.; Ferraris, J. P. *Synth. Met.* 1997, 84, 349.
43. Nishikitani, Y.; Kobayashi, M.; Uchida, S.; Kubo, T. *Electrochim. Acta* 2001, 46, 2035.
44. Desbenemonvernay, A.; Lacaze, P. C.; Cherigui, A. *J. Electroanal. Chem.* 1989, 260, 75.
45. Kulesza, P. J.; Miecznikowski, K.; Chojak, M.; Malik, M. A.; Zamponi, S.; Marassi, R. *Electrochim. Acta* 2001, 46, 4371.
46. Xiong, S.; Phua, S. L.; Dunn, B. S.; Ma, J.; Lu, X. *Chem. Mater.* 2010, 22, 255
47. Higuchi, M.; Akasaka, Y.; Ikeda, T.; Hayashi, A.; Kurth, D. G. *J. Inorg. Organomet. Polym Mater.* 2009, 19, 74.
48. Yu, Y.-H.; Lai, C.-Y.; Chen, C.-L.; Yeh, J.-M. *J. Electron. Mater.* 2006, 35, 1571
49. Jain, V.; Sahoo, R.; Jinschek, J. R.; Montazami, R.; Yochum, H. M.; Beyer, F. L.; Kumar, A.; Heflin, J. R. *Chem. Commun.* 2008, 3663.
50. Wu, C.-G.; Chung, M.-H. *J. Solid State Chem.* 2004, 177, 2285
51. Baek, J.; Kim, Y.; Oh, H.; Kim, E. *Curr. Appl. Phys.* 2009, 9, S110.
52. Syed, A. A.; Dinesan, M. K. *Talanta* 1991, 38, 815
53. Bernard, M. C.; Cordoba-Torresi, S.; Goff, A. H.-L. *Sol. Energy Mater. Sol. Cells* 1992, 25, 225.
54. Kobayashi, T.; Yoneyama, H.; Tamura, H. *J. Electroanal. Chem.* 1984, 161, 419.
55. Panero, S.; Scrosati, B.; Baret, M.; Cecchini, B.; Masetti, E. *Sol. Energ. Mater. Sol. C.* 1995, 39, 239.
56. Zhang, L.; Xiong, S.; Ma, J.; Lu, X. *Sol. Energ. Mat. Sol. C.* 2009, 93, 625.

-
57. Huang, L.-M.; Chen, C.-H.; Wen, T.-C. *Electrochim. Acta* 2006, 51, 5858.
58. Lin, T.-H.; Ho, K.-C. *Sol. Energ. Mater. Sol. C.* 2006, 90, 506.
59. Duek, E. A. R.; Depaoli, M. A.; Mastragostino, M. *Adv. Mater.* 1993, 5, 650.
60. Manisankar, P.; Vedhi, C.; Selvanathan, G.; Somasundaram, R. M. *Chem. Mater.* 2005, 17, 1722.
61. Huang, L. M.; Wen, T.-C.; Gopalan, A. *Synth. Met.* 2002, 130, 155.
62. Louwet, F.; Groenendaal, L.; Dhaen, J.; Manca, J.; Van Luppen, J.; Verdonck, E.; Leenders, L. *Synth. Met.* 2003, 135-136, 115.
63. Sindhu, S.; Rao, K. N.; Ahuja, S.; Kumar, A.; Gopal, E. S. R. *Mat. Sci. Eng. B-Solid* 2006, 132, 39
64. Wang, J. S.; Dunn, B. M.S. *The infrared optical properties and electrochromic device design of PEDOT*. 2006, University of California, Los Angeles, USA.
65. Yang, C. Y.; Smith, P.; Heeger, A. J.; Cao, Y.; Osterholm, J. E. *Polymer* 1994, 35, 1142
66. Kim, J.; Kwon, S.; Ihm, D. *Curr. Appl. Phys.* 2007, 7, 205.
67. Osterholm, J. E.; Cao, Y.; Klavetter, F.; Smith, P. *Synth. Met.* 1993, 55, 1034.
68. Han, M. G.; Cho, S. K.; Oh, S. G.; Im, S. S. *Synth. Met.* 2002, 126, 53.
69. Taka, T.; Laakso, J.; Levon, K. *Solid State Commun.* 1994, 92, 393
70. Yin, W.; Ruckenstein, E. *Synth. Met.* 2000, 108, 39
71. Zagorska, M.; Kulszewicz-Bajer, I.; Blet, O.; Zawirska, P.; Dufour, B.; Rannou, P.; Pron, A. *Synth. Met.* 2003, 138, 543
72. Genoud, F.; Kulszewicz-Bajer, I.; Dufour, B.; Rannou, P.; Pron, A. *Synth. Met.* 2001, 119, 415
73. Yang, Y.; Jiang, Y.; Xu, J.; Yu, J. *Colloids Surf., A* 2007, 302, 157
74. Tang, Z.; Donohoe, S. T.; Robinson, J. A.; Chiarelli, P. A.; Wang, H. L. *Polymer* 2005, 46, 9043

-
75. Pang, Y. H.; Li, X. Y.; Shi, G. Y.; Wang, F.; Jin, L. T. *Thin Solid Films* 2008, 516, 6512.
76. Ahmad, S.; Singh, S. *Electrochem. Commun.* 2008, 10, 895.
77. Hu, C. W.; Lee, K. M.; Huang, J. H.; Hsu, C. Y.; Kuo, T. H.; Yang, D. J.; Ho, K. C. *Sol. Energy Mater. Sol. Cells* 2009, 93, 2102.
78. Hu, C. W.; Lee, K. M.; Vittal, R.; Yang, D. J.; Ho, K. C. *J. Electrochem. Soc.* 2010, 157, P75.
79. Rogers, R. D.; Seddon, K. R. *Science* 2003, 302, 792.
80. Surca Vuk, A.; Jovanovski, V.; Pollet-Villard, A.; Jerman, I.; Orel, B. *Sol. Energ. Mat. Sol. C.* 2008, 92, 126
81. Marcilla, R.; Alcaide, F.; Sardon, H.; Pomposo, J. A.; Pozo-Gonzalo, C.; Mecerreyes, D. *Electrochem. Commun.* 2006, 8, 482.
82. Ma, L.; Li, Y.; Yu, X.; Yang, Q.; Noh, C.-H. *Sol. Energ. Mat. Sol. C.* 2008, 92, 1253.
83. Garcia, B.; Lavalley, S.; Perron, G.; Michot, C.; Armand, M. *Electrochim. Acta* 2004, 49, 4583
84. Wang, P.; Zakeeruddin, S. M.; Comte, P.; Exnar, I.; Gratzel, M. *J. Am. Chem. Soc.* 2003, 125, 1166.
85. Susan, M.; Noda, A.; Mitsushima, S.; Watanabe, M. *Chem. Commun.* 2003, 938.
86. Stenger-Smith, J. D.; Webber, C. K.; Anderson, N.; Chafin, A. P.; Zong, K. K.; Reynolds, J. R. *J. Electrochem. Soc.* 2002, 149, A973.
87. Fuller, J.; Breda, A. C.; Carlin, R. T. *J. Electroanal. Chem.* 1998, 459, 29.
88. Kim, K.-S.; Park, S.-Y.; Choi, S.; Lee, H. *J. Power Sources* 2006, 155, 385.
89. Singh, K. P.; Singh, R. P.; Gupta, P. N. *Solid State Ionics* 1995, 78, 223.
90. Mecerreyes, D.; Marcilla, R.; Ochoteco, E.; Grande, H.; Pomposo, J. A.; Vergaz, R.; Sanchez Pena, J. M. *Electrochim. Acta* 2004, 49, 3555.
91. Leon-Silva, U.; Nicho, M. E.; Hu, H. L.; Cruz-Silva, R. *Sol. Energ. Mat. Sol. C.* 2007, 91, 1444.
92. Bernard, M.-C.; Goff, A. H.-L.; Zeng, W. *Electrochim. Acta* 1998, 44, 781

-
93. Bernard, M.-C.; Hugot-Le Goff, A.; Zeng, W. *Synth. Met.* 1997, 85, 1347.
 94. Rauh, R. D.; Cogan, S. F. *Solid State Ionics* 1988, 28-30, 1707.
 95. Ma, L.; Li, Y.; Yu, X.; Yang, Q.; Noh, C.-H. *Sol. Energ. Mat. Sol. C.* 2009, 93, 564.
 96. Pang, Y.; Li, X.; Ding, H.; Shi, G.; Jin, L. *Electrochim. Acta* 2007, 52, 6172
 97. Pahal, S.; Deepa, M.; Bhandari, S.; Sood, K. N.; Srivastava, A. K. *Sol. Energ. Mat. Sol. C.* 2010, 94, 1064.
 98. Ak, M.; Durmus, A.; Toppare, L. *Solid State Sci.* 2007, 9, 843.
 99. Camurlu, P.; Cirpan, A.; Toppare, L. *J. Electroanal. Chem.* 2004, 572, 61.
 100. Padilla, J.; Seshadri, V.; Otero, T. F.; Sotzing, G. A. *J. Electroanal. Chem.* 2007, 609, 75.
 101. Bulut, U.; Cirpan, A. *Synth. Met.* 2005, 148, 65.
 102. Lim, J. Y.; Ko, H. C.; Lee, H. *Synth. Met.* 2006, 156, 695
 103. Gazotti, W. A.; De Paoli, M. A.; Casalbore-Miceli, G.; Geri, A.; Zotti, G. *J. Appl. Electrochem.* 1999, 29, 753.
 104. Aubert, P. H.; Argun, A. A.; Cirpan, A.; Tanner, D. B.; Reynolds, J. R. *Chem. Mater.* 2004, 16, 2386.
 105. Schwendeman, I.; Hwang, J.; Welsh, D. M.; Tanner, D. B.; Reynolds, J. R. *Adv. Mater.* 2001, 13, 634.
 106. Dyer, A. L.; Grenier, C. R. G.; Reynolds, J. R. *Adv. Funct. Mater.* 2007, 17, 1480.
 107. Decher, G. *Science* 1997, 277, 1232.
 108. Hammond, T. P. *Adv. Mater.* 2004, 16, 1271.
 109. Choi, K.; Yoo, S. J.; Sung, Y. E.; Zentel, R. *Chem. Mater.* 2006, 18, 5823.
 110. Cheung, J. H.; Stockton, W. B.; Rubner, M. F. *Macromolecules* 1997, 30, 2712.
 111. DeLongchamp, D. M.; Hammond, P. T. *Adv. Mater.* 2001, 13, 1455.
 112. Chen, Y.; Wu, J.; Chung, Y. *Biosensors Bioelectron.* 2006, 22, 489.

-
113. Cutler, C. A.; Bouguettaya, M.; Kang, T. S.; Reynolds, J. R. *Macromolecules* 2005, 38, 3068.
114. DeLongchamp, D. M.; Hammond, P. T. *Chem. Mater.* 2004, 16, 4799.
115. DeLongchamp, D. M.; Kastantin, M.; Hammond, P. T. *Chem. Mater.* 2003, 15, 1575.
116. DeLongchamp, D. M.; Hammond, P. T. *Adv. Funct. Mater.* 2004, 14, 224.
117. Baucke, F. G. K. *Mat. Sci. Eng. B* 1991, 10, 285.
118. Rosseinsky, D. R.; Mortimer, R. J. *Adv. Mater.* 2001, 13, 783.
119. Li, H.; Xie, K.; Pan, Y.; Yao, M.; Xin, C. *Synth. Met.* 2009, 159, 1386.
120. Zhang, J.; Lu, F.; Huang, H.; Wang, J.; Yu, H. a.; Jiang, J.; Yan, D.; Wang, Z. *Synth. Met.* 2005, 148, 123.
121. Rougier, A.; Sauvet, K.; Sauques, L. *Ionics* 2008, 14, 99.
122. See the following websites:
<http://www.sage-ec.com>;
<http://www.donnelly.com>;
<http://www.electrochromicink.com>;
<http://www.gentex.com>;
<http://www.ntera.com>;
<http://www.chromogenics.com>;
123. Padilla, J.; Seshadri, V.; Sotzing, G. A.; Otero, T. F. *Electrochem. Commun.* 2007, 9, 1931.
124. Lim, J. Y.; Ko, H. C.; Lee, H. *Synth. Met.* 2005, 155, 595.
125. Fang, Y. K.; Chou, T.-H.; Lin, C.-Y.; Chiang, Y. T.; Chen, S.-F.; Yang, C.-Y.; Chang, S.-H.; Lin, C.-S. *J. Phys. Chem. Solids* 2008, 69, 734.
126. Argun, A. A.; Aubert, P. H.; Thompson, B. C.; Schwendeman, I.; Gaupp, C. L.; Hwang, J.; Pinto, N. J.; Tanner, D. B.; MacDiarmid, A. G.; Reynolds, J. R. *Chem. Mater.* 2004, 16, 4401.
127. Pinheiro, C.; Parola, A. J.; Pina, F.; Fonseca, J.; Freire, C. *Sol. Energ. Mat. Sol. C.* 2008, 92, 980.
128. Rauh, R. D.; Wang, F.; Reynolds, J. R.; Meeker, D. L. *Electrochim. Acta* 2001, 46, 2023.

-
129. Sarac, A. S.; Ates, M.; Kilic, B. *Int. J. Electrochem. Sci.* 2008, 777.
130. Marken, F.; Cromie, S.; Mckee, V. *J. Solid State Electrochem.* 2003, 141.
131. Argun, A. A. *Ph.D thesis. Patterning of conjugated polymers for electrochromic devices.* 2004, University of Florida, USA.
132. Bornstein, J.; Macaione, D. P.; Bergquist, P. R. *Inorg. Chem.* 1985, 24, 625.
133. Kumar, D.; Clair, T. L. S. *Polyhedron* 1992, 11, 1671.
134. Xu, J.; He, C.; Chung, T. S. *J. Polym. Sci. Pol. Chem.* 2001, 39, 2998
135. Alekperov, D.; Shirotsaki, T.; Sakurai, T.; Popova, G.; Kireev, V.; Ihara, H. *Polym. J.* 2003, 35, 417.
136. Sonmez, G.; Meng, H.; Wudl, F. *Chem. Mater.* 2004, 16, 574.
137. Ren, X.; Pickup, P. G. *J. Electroanal. Chem.* 1997, 420, 251.
138. Lu, X.; Tan, C. Y.; Xu, J.; He, C. *Synth. Met.* 2003, 138, 429.
139. Prathab, B.; Subramanian, V.; Aminabhavi, T. M. *Polymer* 2007, 48, 409
140. Barriga, J.; Coto, B.; Fernandez, B. *Tribol. Int.* 2007, 40, 960.
141. Pouget, J. P.; Jozefowicz, M. E.; Epstein, A. J.; Tang, X.; Macdiarmid, A. G. *Macromolecules* 1991, 24, 779
142. Jia, P.; Xu, J.; Ma, J.; Lu, X. *Eur. Polym. J.* 2009, 45, 772.
143. Cao, Y.; Andreatta, A.; Heeger, A. J.; Smith, P. *Polymer* 1989, 30, 2305.
144. Rodrigues, M. A.; De Paoli, M.-A.; Mastragostino, M. *Electrochim. Acta* 1991, 36, 2143.
145. Geng, Y.; Li, J.; Jing, X.; Wang, F. *Synth. Met.* 1997, 84, 81.
146. Stockton, W. B.; Rubner, M. F. *Macromolecules* 1997, 30, 2717
147. Tang, J.; Jing, X.; Wang, B.; Wang, F. *Synth. Met.* 1988, 24, 231
148. Campos, T. L. A.; Kersting, D. F.; Ferreira, C. A. *Surf. Coat. Technol.* 1999, 122, 3.

-
149. Kim, B. S.; Gao, H.; Argun, A. A.; Matyjaszewski, K.; Hammond, P. T. *Macromolecules* 2009, 42, 368.
150. Shreepathi, S.; Holze, R. *Chem. Mater.* 2005, 17, 4078
151. Zlotnikov, I.; Gotman, I.; Gutmanas, E. Y. *Appl. Surf. Sci.* 2008, 255, 3447.
152. Xiong, S.; Jia, P.; Mya, K. Y.; Ma, J.; Boey, F.; Lu, X. *Electrochim. Acta* 2008, 53, 3523
153. Kogan, I. L.; Gedrovich, G. V.; Fokeeva, L. S.; Shunina, I. G. *Electrochim. Acta* 1996, 41, 1833.
154. Grzeszczuk, M.; Poks, P. *Synth. Met.* 1998, 98, 25.
155. Li, C.; Mu, S. *Synth. Met.* 2004, 144, 143.
156. Yang, C. H.; Chih, Y. K.; Wu, W. C.; Chen, C. H. *Electrochem. Solid-State Lett.* 2006, 9, C5.
157. Tian, S.; Baba, A.; Liu, J.; Wang, Z.; Knoll, W.; Park, M. K.; Advincula, R. *Adv. Funct. Mater.* 2003, 13, 473
158. Zhang, N.; Schweiss, R.; Knoll, W. *J. Solid State Electrochem.* 2007, 11, 451.
159. Baba, A.; Park, M. K.; Advincula, R. C.; Knoll, W. *Langmuir* 2002, 18, 4648.
160. Yee, W. A.; Xiong, S.; Ding, G.; Nguyen, C. A.; Lee, P. S.; Ma, J.; Kotaki, M.; Liu, Y.; Lu, X. *Macromol. Rapid Comm.* 2010, 31, 1779.
161. Kang, E. T.; Neoh, K. G.; Tan, K. L. *Synth. Met.* 1995, 68, 141.
162. Nicolau, Y. F.; Ermolieff, A. *Synth. Met.* 1995, 71, 2073.
163. Wei, X.-L.; Fahlman, M.; Epstein, K. J. *Macromolecules* 1999, 32, 3114.
164. Han, M. G.; Im, S. S. *Polymer* 2000, 41, 3253.
165. Jousseume, V.; Morsli, M.; Bonnet, A.; Lefrant, S. *J. Appl. Polym. Sci.* 1998, 67, 1209
166. Chen, S. A.; Hwang, G. W. *J. Am. Chem. Soc.* 1995, 117, 10055.
167. Yue, J.; Epstein, A. J.; Macdiarmid, A. G. *Mol. Cryst. Liq. Cryst.* 1990, 189, 255

168. Jiang, Y.; Epstein, A. J. *J. Am. Chem. Soc.* 1990, 112, 2800.
169. Kang, E. T.; Neoh, K. G.; Woo, Y. L.; Tan, K. L. *Polymer* 1992, 33, 2857.
170. Tzou, K.; Gregory, R. V. *Synth. Met.* 1993, 53, 365
171. Gao, H.; Jiang, T.; Han, B.; Wang, Y.; Du, J.; Liu, Z.; Zhang, J. *Polymer* 2004, 3017.
172. lekha, P. C.; Subramanian, E.; Padiyan, D. P. *Sens. Actuators, B* 2007, 122, 274.
173. De, S.; Dey, A.; De, S. K. *J. Phys. Chem. Solids* 2007, 68, 66.
174. Subramanian, S.; Chithra lekha, P.; Pathinettam Padiyan, D. *Curr. Appl. Phys.* 2009, 9, 1140
175. Yakuphanoglu, F.; Senkal, B. F.; Sarac, A. *J. Electron. Mater.* 2008, 37, 930.
176. Pei, Q.; Zuccarello, G.; Ahlskog, M.; Inganäs, O. *Polymer* 1994, 35, 1347.
177. Radhakrishna, S.; Chowdari, B. V. R.; Viswanath, A. K. *Chem. Phys. Lett.* 1976, 44, 121.
178. Sakamaki, K.; Akagi, K.; Shirakawa, H.; Kyotani, H. *Synth. Met.* 1997, 84, 365.

LIST OF PUBLICATIONS

1. **Jia, P.**; Argun, A. A.; Xu, J.; Xiong, S.; Ma, J.; Hammond, P. T.; Lu, X. "High-contrast electrochromic thin films via layer-by-layer assembly of star-like and sulfonated polyaniline", *Chemistry of Materials* 2010, 22, 6085-6091.
2. **Jia, P.**; Argun, A. A.; Xu, J.; Xiong, S.; Ma, J.; Hammond, P. T.; Lu, X. "Enhanced electrochromic switching in multilayer thin films of polyaniline-tethered silsesquioxane nanocage", *Chemistry of Materials* 2009, 21, 4434-4441.
3. Wang, X.*; Ng, J.*; **Jia, P.***; Lin, T.; Cho, C.; Xu, J.; Lu, X.; He, C. "Synthesis, electronic, and emission spectroscopy, and electrochromic characterization of azulene-fluorene conjugated oligomers and polymers", *Macromolecules* 2009, 42, 5534-5544. (*equal contribution)
4. **Jia, P.**; Ma, J.; Xu, J.; Lu, X. "Enhancement of electrochromic contrast by tethering polyaniline onto cyclotriphosphazene", *European Polymer Journal* 2009, 45, 772-778.
5. Xiong, S.; **Jia, P.**; Mya, K. Y.; Ma, J.; Boey, F.; Lu, X. "Star-like polyaniline prepared from octa(aminophenyl) silsesquioxane: enhanced electrochromic contrast and electrochemical stability", *Electrochimica Acta* 2008, 53, 3523-3530.
6. Xiong, S.; Wei, J.; **Jia, P.**; Yang, L.; Ma, J.; Lu, X. "Water-processable polyaniline with bonded single-walled carbon nanotubes: enhanced electrochromic properties and impedance analysis", submitted.
7. **Jia, P.**; Yee, W. A.; Xu, J.; Toh, C. L.; Ma, J.; Lu, X. "Supercritical CO₂-treated electrospun poly(vinylidene fluoride) membranes as ionic-liquid host in electrochromic devices", in preparation.
8. Yee, W. A.; **Jia, P.**; Zhang, C.; Kong, J.; Masaya, K.; Liu, Y.; Lu, X. "Electrospinning of poly(vinylidene fluoride) with carbon nanotubes II: effects of functional groups on interfacial interaction affecting crystalline structures", in preparation.