Novel High-T_g and Thermally Stable Polyimides Featuring Electroactive Diphenylpyrenylamine Groups

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ABSTRACT

A novel class of polyimides with the electroactive diphenylpyrenylamine unit were prepared from the polycondensation reactions of a newly synthesized diamine monomer, i.e., 1-[N,N-di(4-aminophenyl)amino]pyrene (2), with aromatic or alicyclic tetracarboxylic dianhydrides via the conventional two-step polycondensation reaction. All polymers exhibited good solubility in many polar organic solvents and could afford robust films via solution casting. In addition to high T_g values and good thermal stability, these polymers also showed useful HOMO energy levels, strong blue light-emitting fluorescence and interesting electrochromic characteristics.
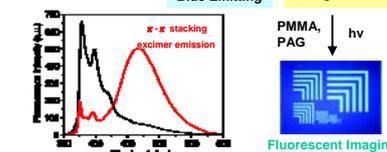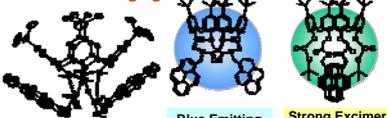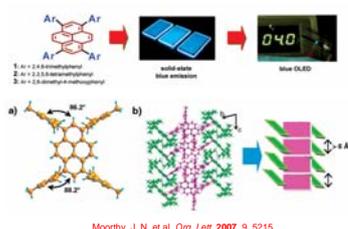
INTRODUCTION

Why focus on Pyrene?

Useful properties of pyrene : (a) high PL efficiency, (b) high carrier mobility, and (c) good hole-injection ability.

A major problem of pyrene derivatives as light emitting materials: Their emission in the solid state is effectively suppressed due to the formation of excimers via π-π stacking.
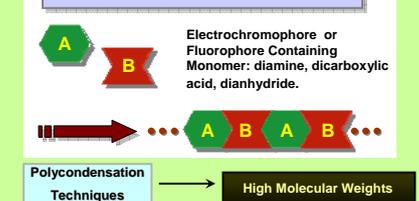
Steric Inhibition of π-Stacking: 1,3,6,8-Tetraarylpyrenes as Efficient Blue Emitters in Organic Light Emitting Diodes (OLEDs)

Moorthy, J. N. et al. *Org. Lett.* **2007**, 9, 5215.

An excimer emission approach for patterned fluorescent imaging

Blue Emitting | Strong Excimer

π-π stacking excimer emission

PMMA, PAG | hv

Fluorescent Imaging

Kim, J. M and Kim, J.S. et al. *Chem. Commun.* **2005**, 3427.

Strategy for High Performance Polymers

Electrochromophore or Fluorophore Containing Monomer: diamine, dicarboxylic acid, dianhydride.

Polycondensation Techniques → High Molecular Weights
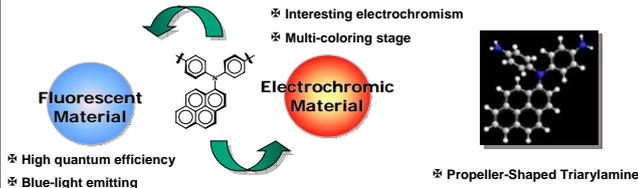
High Contrast Ratio and Rapid Switching Electrochromic Polymeric Films Based on 4-(Dimethylamino)triphenylamine-Functionalized Aromatic Polyamides
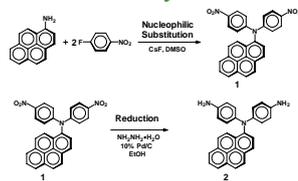
(NMe_2TPA-functionalized aromatic polyamides)

Hsiao, S.-H; Liou, G.-S.; Kung, Y.-C.; Yen, H.-J. *Macromolecules* **2008**, 41, 2800.

MOTIVATION AND MOLECUAR DESIGN

✠ Interesting electrochromism
✠ Multi-coloring stage

Fluorescent Material ⇄ Electrochromic Material

✠ High quantum efficiency
✠ Blue-light emitting

✠ Propeller-Shaped Triarylamine
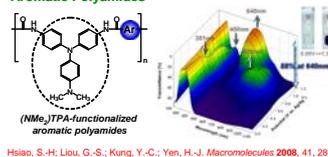
EXPERIMENTAL

Monomer Synthesis

Nucleophilic Substitution — CsF, DMSO

Reduction — $NH_2NH_2 \cdot H_2O$, 10% Pd/C, EtOH

Polymer Synthesis

1. DMAc, r.t.
2. -H_2O

Ar =
a b c d
e f g

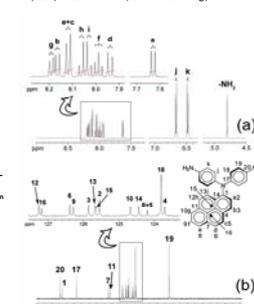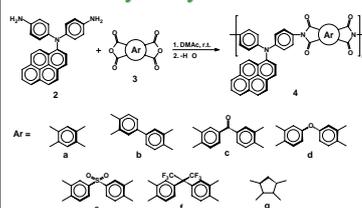### Structural Characterization

Diphenylpyrenylamine-Based Diamine (yellow fine crystal)
yield: 75 %. mp: 227-229 °C (DSC, 2 °C/min).
IR (KBr): 3200-3400 (N-H stretching).

Figure 1. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of diamine monomer **2** in DMSO-d_6.

RESULTS AND DISCUSSION

Table 1. Thermal properties of the polyimides[a]

Polymer Code	T_g (°C)[b]	T_d at 10 wt% loss (°C)[c] In N_2	In air	Char yield (%)[d]
4a	- (-)[e]	626 (606)	600 (596)	68.7
4b	364 (331)	631 (613)	614 (611)	77.7
4c	349 (309)	609 (590)	607 (590)	72.0
4d	333 (295)	620 (608)	603 (591)	73.9
4e	346 (326)	587 (546)	579 (577)	69.2
4f	349 (316)	594 (581)	577 (571)	70.0
4g	281 (-)	552 (-)	481 (-)	56.1

[a] The polymer film samples were heated at 300 °C for 1 hr prior to all the thermal analyses. [b] Determined from the DSC heating traces with a heating rate of 20 °C/min in nitrogen. The midpoint temperature of the baseline shift on the DSC trace was defined as T_g. [c] Decomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C/min. [d] Residual weight percentages at 800 °C under a nitrogen flow. [e] Values shown in parentheses are those of structurally similar polyimides 4'.

Table 2. Optical properties of the polyimides

Polymer code	In solution Abs λ_{max} (nm)[a]	FL λ_{max} (nm)[b]	Φ_{FL} (%)[c]	As film Abs λ_{max} (nm)	Abs λ_{onset} (nm)
4a	317, 361	420	0.42 (0.12)	316, 382	464
4b	328, 378	422	0.20 (0.11)	318, 382	468
4c	315, 378	415	0.28 (0.13)	316, 382	462
4d	327, 380	426	0.31 (0.14)	328, 382	457
4e	329, 378	422	0.42 (0.11)	330, 382	460
4f	329, 378	418	0.82 (0.12)	329, 382	459
4g	315, 379	474	43.8 (6.33)	325, 382	442

[a] UV/vis absorption measured in dilute NMP solution (about 10^{-5} mol/L). [b] Excited at absorption λ_{max}. [c] Fluorescence quantum yield, using 9,10-diphenylanthracene as a standard (Φ_{FL} = 90%, in cyclohexane). Values shown in the parentheses are those of structurally similar polyimides 4'.

Table 3. Optical properties of the polyimides **4g** in various solvents[a]

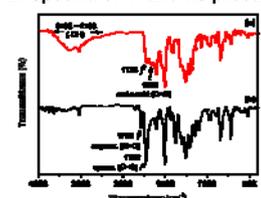| Solvents	ε[b]	Abs λ_{max} (nm)	FL λ_{max} (nm)[c]	Φ_{FL} (%)[d]	FWHM (nm)[e]
Toluene	2.4	316, 382	442	55.4	55
CHCl$_3$	4.8	313, 378	445	53.3	60
THF	7.5	316, 379	459	50.5	63
NMP	32.2	315, 379	474	43.8	75
DMSO	47.0	318, 379	478	43.1	76

[a] Measured at a polymer concentration of ca. 10^{-5} M. [b] Dielectric constant of the solvent. [c] Excited at the absorption maximum for solution states. [d] The fluorescence quantum yields determined by an integrating sphere, using 9,10-diphenylanthracene as a standard (Φ_{FL} = 90%, measured in dilute cyclohexane solution). [e] FWHM = Full-width at half-maximum.

**Table 4.** Redox potentials and energy levels of polyimides

Polymer Code	Oxidation Potential (V)[a] E_{onset}	$E_{1/2}$[b]	E_g^{opt} (eV)[c]	E_{HOMO} (eV)[d]	E_{LUMO} (eV)[e]
4a	0.90	1.00 (1.17)[f]	2.67	5.36	2.69
4b	0.96	1.11 (1.17)	2.65	5.51	2.86
4c	0.97	1.10 (1.17)	2.68	5.47	2.79
4d	0.97	1.00 (1.14)	2.71	5.36	2.65
4e	0.97	1.14 (1.17)	2.70	5.50	2.80
4f	0.89	1.00 (1.18)	2.70	5.36	2.66
4g	0.96	1.04 (-)	2.81	5.40	2.59

[a] vs. Ag/AgCl in CH_3CN. [b] $E_{1/2}$: an average of the redox peak potentials. [c] Optical band gap, derived from the observed optical edge: E_g^{opt} = 1240/λ_{onset}. [d] HOMO energy was calculated with reference to ferrocene (4.8 eV). [e] LUMO energy was derived from the relation, E_{LUMO} = E_{HOMO} - E_g^{opt}. [f] Values shown in parentheses are those of structurally similar polyimides 4'.
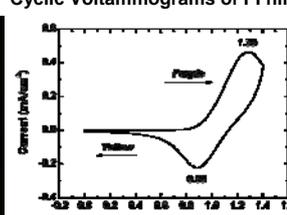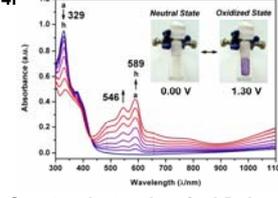
IR spectra of 4f and its precursor
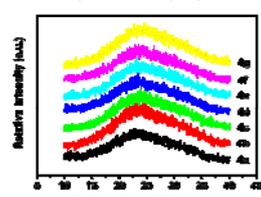
DSC Curve of 4b

Solvatochromism of 4g
UV-irradiated 365 nm
a b c d e
Solvatochromism
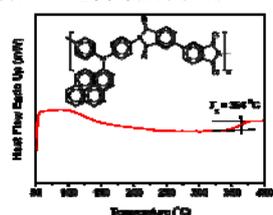
Cyclic Voltammograms of PI film 4f
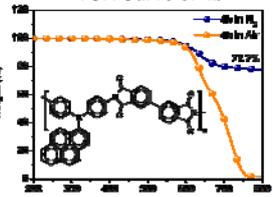Neutral State | Oxidized State
0.00 V | 1.30 V

Spectroelectrochemical Behavior
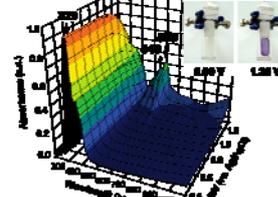
XRD pattern of polyimides

TGA Curve of 4b

Normalized FL spectra of 4g
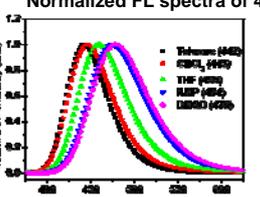
Redox Mechanism of PI
Neutral State
-1e
Oxidized State

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Novel High-T_g and Thermally Stable Polyimides Featuring Electroactive Diphenylpyrenylamine Groups

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Abstract

A novel class of polyimides with the electroactive diphenylpyrenylamine unit were prepared from the polycondensation reactions of a newly synthesized diamine monomer, i.e., 1-[*N,N*-di(4-aminophenyl)amino]pyrene (**2**), with aromatic or alicyclic tetracarboxylic dianhydrides via the conventional two-step polycondensation reaction. All polymers exhibited good solubility in many polar organic solvents and could afford robust films via solution casting. In addition to high T_g values and good thermal stability, these polymers also showed useful HOMO energy levels, strong blue light-emitting fluorescence and interesting electrochromic characteristics.

1. Introduction

Flat π-conjugated polycyclic aromatic hydrocarbons are in general highly fluorescent and find many optoelectronic applications.[1] However, a well-known problem with these systems is that their emission in the solid state is effectively suppressed due to the formation of excimers via π-π stacking. For example, pyrene, a flat aromatic molecule, exhibits efficient fluorescence property, and the emission is pure blue to permit ready exploitation as a blue-light emitting material in organic light emitting diodes (OLEDs).[2] Many pyrene derivatives have been used in OLEDs in order to improve hole transporting ability because of the electron-rich property of the pyrene moiety.[3,4] However, the high tendency towards π-π stacking of the pyrene moieties generally lends the pyrene-containing emitters strong intermolecular interactions in the solid state, which leads to a substantial red shift of their fluorescence emission and a decrease of the fluorescence quantum yields. It has been demonstrated that the pyrenes functionalized by sterically hindered aryl rings do not undergo close π-stacking leading to solid-state emission properties that parallel those in the solution state.[5] In addition, diarylamino functionalized pyrene derivatives have been found to perform efficiently as bright blue emitters and charge transport materials in OLEDs.[6] Triarylamine derivatives are well known for photo- and electroactive properties that find optoelectronic applications as photoconductors, hole-transporters, and light-emitters. Triarylamines can be easily oxidized to form stable radical cations, and the oxidation process is always associated with a noticeable change of coloration. Thus, many triarylamine-based electrochromic polymers have been reported in literature.[7,8]

Aromatic polyimides are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties.[9] However, rigidity of the backbone and strong interchain interactions result in high melting or glass-transition temperatures (T_g) and limited solubility in most organic solvents. These properties make them generally intractable or difficult to process, thus restricting their wide-spread applications. To overcome such a difficulty, polymer-structure modification becomes necessary. One of the common approaches for increasing solubility and processability of aromatic polyimides without sacrificing high thermal stability is the introduction of bulky, packing-disruptive groups into the polymer backbone. In recent years, we have developed a number of high-performance polymers (e.g., aromatic polyamides and polyimides) carrying the triarylamine unit as an electrochromic functional moiety.[10-15] Our strategy was to synthesize the triarylamine-containing monomers such as diamines and dicarboxylic acids that were then reacted with the corresponding co-monomers through conventional polycondensation techniques. The obtained polymers possessed characteristically high molecular weights and high thermal stability. Because of the incorporation of packing-disruptive, propeller-shaped triarylamine units along the polymer backbone, most of these polymers exhibited good solubility in polar organic solvents. They may form uniform, transparent amorphous thin films by solution casting and spin-coating methods. This is advantageous for their ready fabrication of large-area, thin-film devices.

Herein we report the synthesis of the new diamine monomer **2** and its derived polyimides containing the bulky diphenylpyrenylamine (DPPA) chromophore. The thermal, fluorescent, electrochemical, and electrochromic properties of these polymers are also presented and compared with those of structurally related ones from 4,4'-diaminotriphenylamine.

2. Monomer synthesis

The new diamine monomer **2** containing a diphenylpyrenylamine unit was synthesized by the synthetic route outlined in Scheme 1. The target diamine monomer **2** was prepared by hydrazine Pd/C-catalyzed reduction of 1-[*N,N*-di(4-nitrophenyl)amino]pyrene (**1**) resulting from *N,N*-diarylation of 1-aminopyrene with *p*-fluoronitrobenzene in the presence of cesium fluoride (CsF). Figure 1 illustrates the ^{1}H NMR and ^{13}C NMR spectra of the diamine monomer **2**. Assignments of each carbon and hydrogen are assisted by the two-dimensional (2-D) COSY NMR spectra, and these spectra are in good agreement with the proposed molecular structure of **2**.
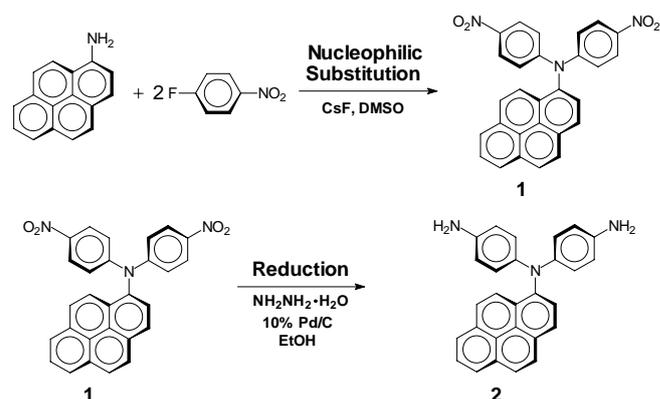
Scheme 1. Synthetic route to the diamine monomer **2**.

3. Polymer synthesis

Polyimides **4a-4g** were prepared in conventional two-step method by the reactions of equal molar amounts of diamine **2** with various tetracarboxylic dianhydrides (**3a** to **3g**) to form poly(amic acid)s, followed by thermal or chemical cyclodehydration (Scheme 2). The inherent viscosities of the wholly aromatic poly(amic acid) precursors were in the range 1.46-2.02 dL/g, indicating the formation of high-molecular-weight polymers. All of these poly(amic acid)s could be cast into flexible and tough films, which were subsequently converted into tough polyimide films.
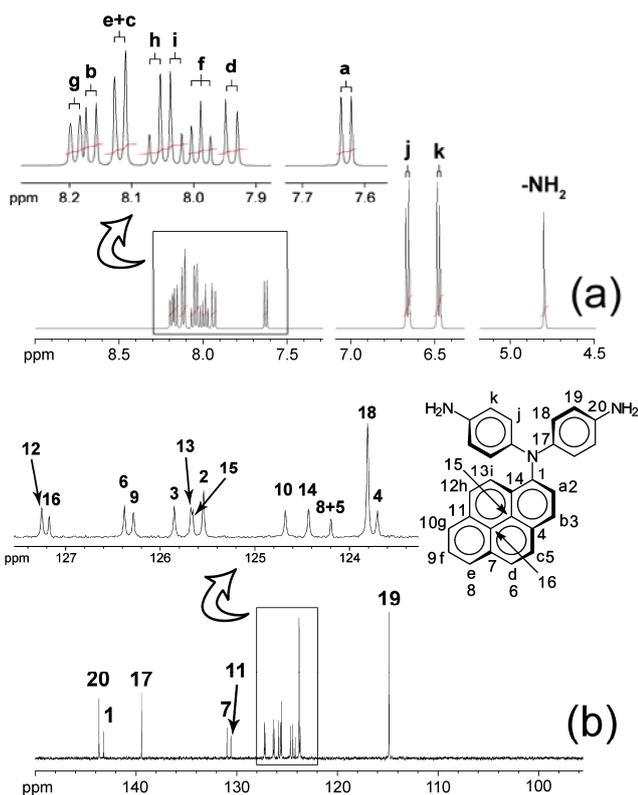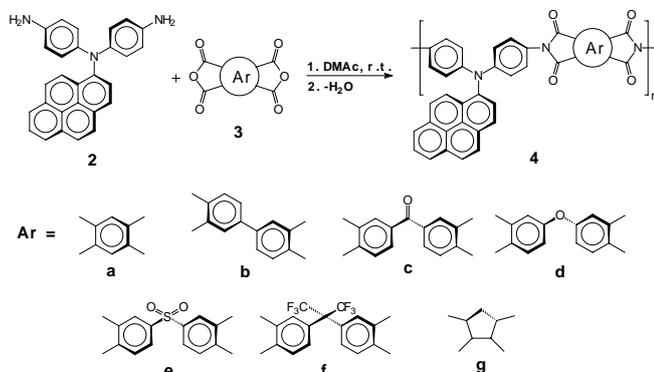
Figure 1. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of diamine monomer **2** in DMSO-d_6.

Scheme 2. Synthesis of polyimides.

4. Organo-solubility and thermal properties

All the polyimides were readily soluble in amide-type polar aprotic solvents (such as NMP, DMAc, and DMF). The high solubility of these polymers is apparently due in part to the presence of the packing-disruptive diphenylpyrenylamine unit in the polymer backbone, which resulted in increased chain packing distances and decreased intermolecular interactions.
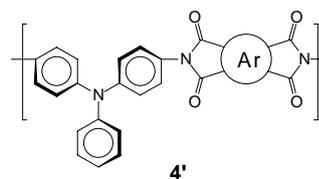
Thermal properties of all the polyimides were evaluated by DSC and TGA techniques. The thermal behavior data of these polymers are summarized in Table 1. The glass-transition temperatures (T_g) of wholly aromatic ones of the prepared polyimides were observed in the range of 333-364 ^{o}C by DSC. Polyimide **4a** did not reveal discernible glass transition on its DSC thermograms possibly because of the high rigidity of its backbone. The 10 % weight-loss temperatures (T_d) of the wholly aromatic polyimides in nitrogen and air were recorded in the range of 587-631 ^{o}C and 577-614 ^{o}C, respectively. The amount of carbonized residue (char yield) of

these polymers was more than 69 % at 800 ^{o}C in nitrogen. Apparently, the high char residues of these aromatic polyimides can be explained by their high aromatic contents in their polymer chains. The lower T_g and T_d values of polyimide **4g** were reasonable when considering the less rigid and less thermally stable aliphatic segment. When compared with the analogous **4'** series polyimides, the **4** series polyimides showed an enhanced T_g and thermal stability. This can be attributed to the presence of rigid pyrene segment.

Table 1. Thermal properties of the polyimides[a]

Polymer code	T_g (^{o}C)[b]	T_d at 10 wt% loss (^{o}C)[c]		Char yield (%)[d]
		In N$_2$	In air	
4a	- (-)[e]	626 (606)	600 (596)	68.7
4b	364 (331)	631 (613)	614 (611)	77.7
4c	349 (309)	609 (590)	607 (590)	72.0
4d	333 (295)	620 (608)	603 (591)	73.9
4e	346 (326)	587 (546)	579 (577)	69.2
4f	349 (316)	594 (581)	577 (571)	70.0
4g	281 (-)	552 (-)	481 (-)	56.1

[a] The polymer film samples were heated at 300 ^{o}C for 1 h prior to all the thermal analyses. [b] Determined from the DSC heating traces with a heating rate of 20 ^{o}C/min in nitrogen. The midpoint temperature of the baseline shift on the DSC trace was defined as T_g. [c] Decomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 ^{o}C/min. [d] Residual weight percentages at 800 ^{o}C under a nitrogen flow. [e] Values shown in parentheses are those of structurally similar polyimides **4'**.

4'

5. Absorption and fluorescence

All the polyimides were examined both by UV-Vis absorption and fluorescence (FL) spectroscopy in solution and in solid state, and the results are presented in Table 2. These polyimides in dilute NMP solution exhibited strong UV-vis absorption bands around 315-329 nm, assignable to that arising from the pyrene based π-π* transitions resulting from the conjugated diphenylpyrenylamine (DPPA) unit. All polyimides also displayed a long wavelength absorption maximum at *ca* 380 nm. This bathochromically shifted transition may be ascribed to that originating from the amine to pyrene charge transfer state.[6] Solid state absorption spectra of these polyimides were very similar to those observed in the solution state, suggesting that the aryl rings do not undergo close π-stacking. These polyimides in dilute NMP solution emitted deep blue to cyan fluorescence; their emission maxima lie in the region between 415 and 474 nm. The fluorescence quantum yields (Φ_{FL}) of these polyimides in NMP solution were found to vary from 0.20% to 43.8%. The low Φ_{FL} of the aromatic polyimides **4a-4f** may be attributed to the quenching effect arising from intra- and interchain charge transfer (CT) complexing between the DPPA donor and the phthalimide acceptor. It is worth noting that CT-inhibited polyimide **4g** derived from alicyclic dianhydride **3g** had a much higher PL quantum yield of 43.8%, similar to those reported for the pyrene-based triarylamines.[6] The diminished CT interaction of semi-aromatic polyimide **4g** also reflected in a lighter color of its cast film as compared with the wholly aromatic ones. As shown in Table 2, the thin film of **4g** had a lower absorption onset wavelength than the other polyimides. When compared with the **4'** series counterparts, the higher quantum efficiency in the **4** series polyimides could be attributable to the presence of rigid, highly fluorescent pyrene chromophore.

Table 2. Optical properties of the polyimides

Polymer code	In solution			As film	
	Abs λ_{max} (nm)[a]	FL λ_{max} (nm)[b]	Φ_{FL} (%)[c]	Abs λ_{max} (nm)	Abs λ_{onset} (nm)
4a	317, 361	420	0.42 (0.12)	316, 382	464
4b	328, 378	422	0.20 (0.11)	318, 382	468
4c	315, 378	415	0.28 (0.13)	316, 382	462
4d	327, 380	426	0.31 (0.14)	328, 382	457
4e	329, 378	422	0.42 (0.11)	330, 382	460
4f	329, 378	418	0.82 (0.12)	329, 382	459
4g	315, 379	474	43.8 (6.33)	325, 382	442

[a] UV/vis absorption measured in dilute NMP solution (about 10^{-5} mol/L).
[b] Excited at absorption λ_{max}. [c] Fluorescence quantum yield, using
9,10-diphenylanthracene as a standard (Φ_{FL} = 90%, in cyclohexane). Values
shown in the parentheses are those of structurally similar polyimides **4'**.

6. Fluorescence solvatochromism

It is known that pyrene derivatives exhibited environment sensitive solvatochromic behavior in which the relative intensity of emission bands is dependent on the solvent polarity.[16,17] In order to investigate the solvatochromic properties, we investigated the absorption and fluorescence of polyimide **4g** in various solvents with different polarity. Figure 2 showed the normalized FL spectra of polyimide **4g** in dilute solution in various solvents, together with fluorescent images of these polymer solutions under UV light irradiation. The absorption and FL emission data are collected in Table 3. In general, the absorption wavelengths for **4g** are not very sensitive to the solvent polarity; this clearly indicates that the solvent polarity did not alter significantly the electronic ground state of this polymer in these solvents. In contrast, the FL emission spectra of **4g** show strong solvent-polarity dependence, revealing a dominant broad emission band that undergoes remarkable bathochromic shifts with an increase of the solvent polarity. A decreased fluorescence quantum yield and an increased band width were also observed in the solvent of higher polarity. The solvatochromic shift could be attributed to the fast intramolecular charge-transfer process resulting in a large change of dipole moment in the excited state.[18] Evidently the amine to pyrene charge transfer state is the excited state in this series polyimides which will be somewhat polar in nature. It has been demonstrated that some triarylamine derivatives possessing a strong donor (amine) and acceptor (such as oxadiazole) exhibit a larger solvatochromic effect in emission.[19,20]

Table 3. Optical properties of polyimide **4g** in various solvents[a]

Solvents	ε[b]	Abs λ_{max} (nm)	FL λ_{max} (nm)[c]	Φ_{FL} (%)[d]	FWHM (nm)[e]
Toluene	2.4	316, 382	442	55.4	55
CHCl₃	4.8	313, 378	445	53.3	60
THF	7.5	316, 379	459	50.5	63
NMP	32.2	315, 379	474	43.8	75
DMSO	47.0	318, 379	478	43.1	76

[a] Measured at a polymer concentration of ca. 10^{-5} M. [b] Dielectric constant of the solvent. [c] Excited at the absorption maximum for solution states. [d] The fluorescence quantum yields determined by an integrating sphere, using 9,10-diphenylanthracene as a standard (Φ_{FL} = 90%, measured in dilute cyclohexane solution). [e] FWHM = Full-width at half-maximum.
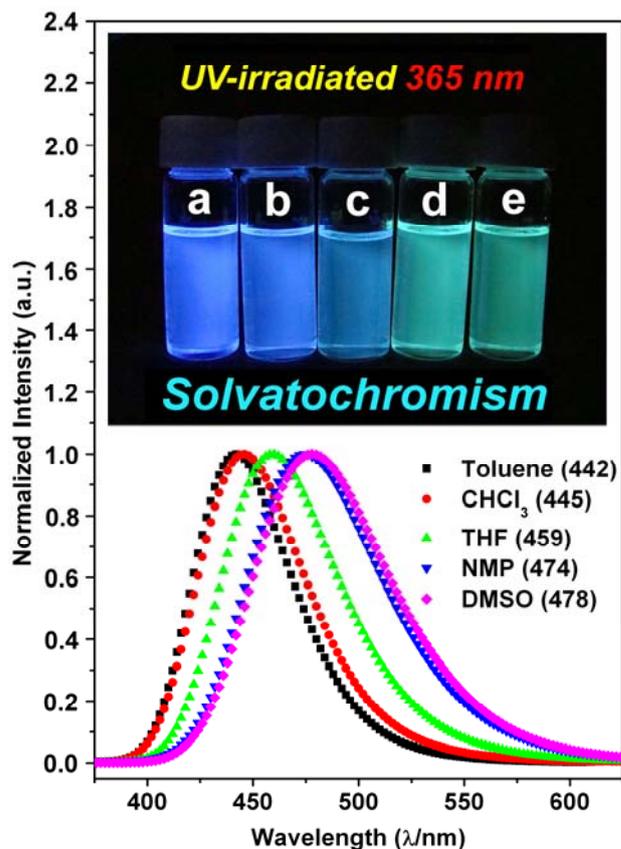

Figure 2. Normalized FL spectra of the dilute solutions (ca. 10^{-5} M) of polyimide **4g** in different solvents: (a) toluene, (b) CHCl₃, (c) THF, (d) NMP, (e) DMSO. Photographs show the appearance of the polymer solutions on exposure to a standard laboratory UV lamp (excited by the 365 nm light).

7. Electrochemical properties

Electrochemical properties of the polyimides were investigated by cyclic voltammetry (CV) conducted for the cast film on the ITO-coated glass substrate as the working electrode in dry acetonitrile (CH₃CN) containing 0.1 M of tetrabutylammonium perchlorate (TBAP) as an electrolyte under nitrogen atmosphere. The redox potentials of these polyimides are collected in Table 4. All the polyimides underwent a reversible one-electron oxidation originating from the pyrenylamine segment. Figure 3 shows a typical CV curve for the representative polyimide **4f**. There is one reversible oxidation redox couple at half-wave potential ($E_{1/2}$) of 1.00 V for polyimide **4f** in the oxidative scan. These polymers exhibited oxidation onset potentials (E_{onset}) and $E_{1/2}$ values in the range of 0.89~0.97 V and 1.00~1.14 V, which are lower than those of the corresponding **4'** counterparts. The decreased oxidation potentials of these polymers should be a result of the incorporation of the electron-rich pyrene moiety. While the energy values of the highest occupied molecular orbital (HOMO) of the corresponding polymers were derived from the oxidation onset potentials, those of the lowest unoccupied molecular orbital (LUMO) were calculated by subtracting the corresponding optical band gap energies from the HOMO values. Assuming that the HOMO energy level for the ferrocene/ferrocenium (Fc/Fc⁺) standard is 4.80 eV with respect to the zero vacuum level, the HOMO and LUMO values for these polyimides vary from 5.36 to 5.47 eV and 2.59 to 2.86 eV, respectively.

Table 4. Redox potentials and energy levels of the polyimides

Polymer Code	Oxidation Potential (V)[a]		E_g^{opt} (eV)[c]	E_{HOMO} (eV)[d]	E_{LUMO} (eV)[e]
	E_{onset}	$E_{1/2}{}^b$			
4a	0.90	1.00 (1.17)[f]	2.67	5.36	2.69
4b	0.96	1.11 (1.17)	2.65	5.51	2.86
4c	0.97	1.10 (1.17)	2.68	5.47	2.79
4d	0.97	1.00 (1.14)	2.71	5.36	2.65
4e	0.97	1.14 (1.17)	2.70	5.50	2.80
4f	0.89	1.00 (1.18)	2.70	5.36	2.66
4g	0.96	1.04 (-)	2.81	5.40	2.59

[a] vs. Ag/AgCl in CH$_3$CN. [b] $E_{1/2}$: an average of the redox peak potentials. [c] Optical band gap, derived from the observed optical edge; $E_g^{opt} = 1240/\lambda_{onset}$. [d] HOMO energy was calculated with reference to ferrocene (4.8 eV). [e] LUMO energy was derived from the relation, $E_{LUMO} = E_{HOMO} - E_g^{opt}$. [f] Values shown in parentheses are those of structurally similar polyimides **4'**.
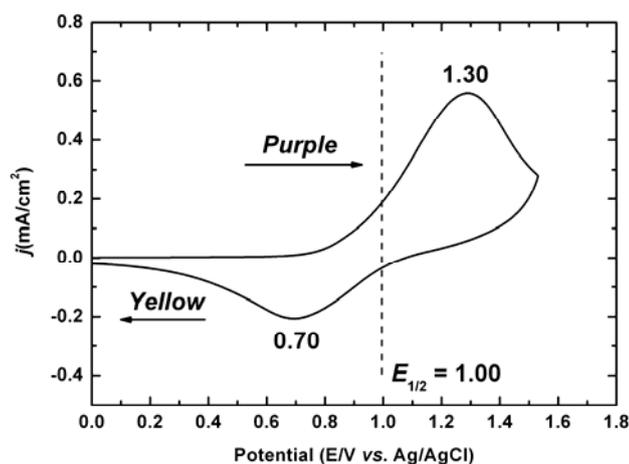

Figure 3. Cyclic voltammogram of the cast film of polyimide **4f** on the ITO-glass substrate in acetonitrile containing 0.1 M TBAP at a scan rate of 50 mV/s.

8. Spectroelectrochemical and electrochromic properties

Spectroelectrochemical experiments were conducted to elucidate the optical characteristics of the electrochromic films. Typical result of the film of polyimide **4f** is presented in Figure 4 as a series of UV-vis-NIR absorbance curves correlated to electrode potentials. In the neutral form, at 0 V, the film exhibited strong absorption at wavelength around 329 nm, characteristic for triarylamine, but it was almost transparent in the visible region. Upon oxidation of the **4f** film (increasing applied voltage from 0 to 1.3 V), the intensity of the absorption peak at 329 nm gradually decreased while new peaks at 546 and 589 nm gradually increased in intensity, and the color of the film changed to purple. We attribute this spectral change to the formation of a monocation radical of the pyrenylamine moiety.

9. Conclusions

A new series of thermally stable and electroactive polyimides with diphenylpyrenylamine core have been synthesized. All the polymers could form morphologically stable and uniform amorphous films using solution-casting techniques. In addition to high T_g, high thermal stability and excellent fluorescent properties (for the semi-aromatic polyimide), the polymers also revealed electrochromic characteristics with color change from pale yellow neutral state to purple oxidized state. Thus, these high performance polymers may find optoelectronic applications as new hole-transporting, light-emitting, and electrochromic materials.
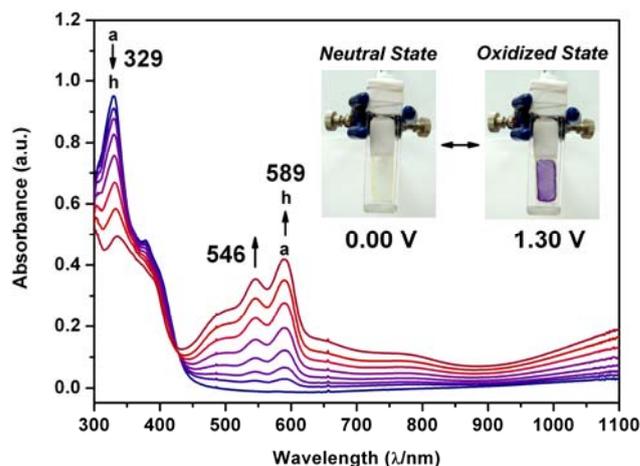

Figure 4. Spectral change of **4f** thin film on the ITO-coated glass substrate (in CH$_3$CN with 0.1 M TBAP as the supporting electrolyte) along with increasing of the applied voltage potentials of (a) 0, (b) 0.95, (c) 1.00, (d) 1.05, (e) 1.10, (f) 1.15, (g) 1.20, (h) 1.30 V vs Ag/AgCl couple as reference. The inset shows the electrochromic photographic images of the film at indicated applied voltages.

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