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Facile preparation of electrochromic poly(amine-imide) films from diimide compounds with terminal triphenylamino groups via electrochemical oxidative coupling reactions

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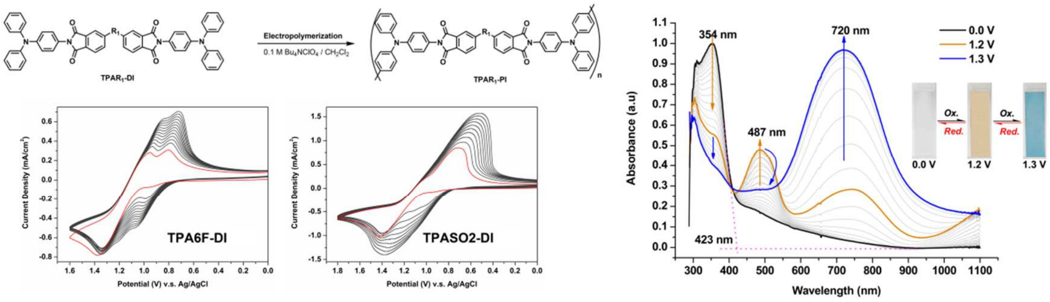
Graphical Abstract

Electroactive and electrochromic poly(amine-imide) films could be directly prepared on electrodes from diimide compounds **TPA6F-DI** and **TPASO2-DI** with triphenylamino end groups by electrochemical oxidative coupling.



Facile preparation of electrochromic poly(amine-imide) films from diimide compounds with terminal triphenylamino groups via electrochemical oxidative coupling reactions

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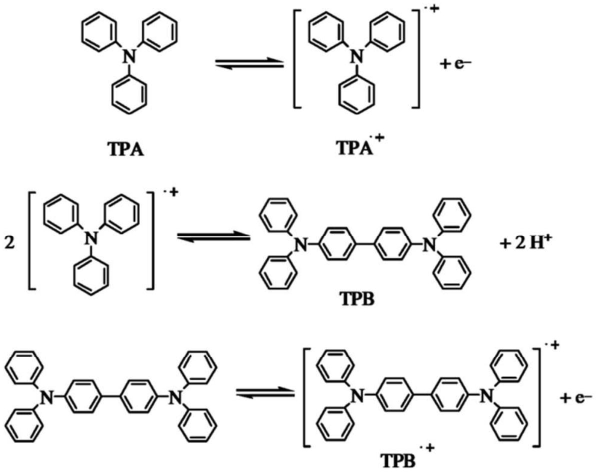
(Abstract)

Two diamide compounds **TPABP-DA** and **TPASO2-DA** and two diimide compounds **TPA6F-DI** and **TPASO2-DI** with triphenylamine (TPA) end groups were synthesized from the condensation reactions of 4-aminotriphenylamine with respective aromatic dicarboxylic acids and tetracarboxylic dianhydrides. The diimide compounds can be electropolymerized into poly(amine-imide) films on the electrode surface in an electrolyte solution via the coupling reactions between the TPA radical cations. In contrast, electro-oxidation of the diamide analogs produced stable TPA radical cations that did not undergo electropolymerization reactions. The elecrtrogenerated films of **TPA6F-DI** and **TPASO2-DI** showed a reversible oxidation redox couple with a half-wave potential ($E_{1/2}$) of 0.96 V on their cyclic voltammograms. They exhibited stable electrochromic properties, with coloration change from a colorless neutral state to orange as a radical cation and blue when fully oxidized.

Introduction

Electrochromic materials have the ability of changing their optical properties as persistent and reversible response by alternation of the applied potential.[1] They have received tremendous interest, due to potential applications in displays, smart windows, and other electrochromic devices.[2] Up to now, many different types of organic and inorganic electrochromic materials[3-6] have been developed, such as inorganic metal oxide, mixed-valence metal complexes, organic small molecules, and conjugated polymers. Electrochromic polymers have received increasing attention due to their fine-tunability of the band gap, high coloration efficiency, fast switching speeds, high contrast ability, and easily processing.[7,8]

Triarylamine derivatives are well-known for their electroactive and photoactive properties that may find optoelectronic applications as photoconductors, hole-transporters, and light-emitters.[9,10] Triarylamines can be easily oxidized to form stable radical cations as long as the *para*-position of the phenyl rings is protected, and the oxidation process is always associated with a strong change of coloration. In recent years, a huge amount of high-performance polymers (typically, aromatic polyamides and polyimides) carrying the triarylamine unit have been prepared and evaluated for electrochromic applications.[11-13] Unsubstituted triphenylamine (**TPA**) undergoes dimerization to tetraphenylbenzidine (**TPB**) after the formation of an unstable monocation radical as shown in **Scheme 1**.[14] This is accompanied by the loss of two protons per dimer and the dimer is more easily oxidized than TPA and also can undergo further oxidations in two discrete one-electron steps to give $TPB^{+\bullet}$ and finally the quinoidal TPB^{+2}. Quantitative data have been obtained for several 4-substituted triphenylamines in the form of second-order coupling rate constants, and it was generally found that electron-donating substituentents such as methoxy group tended to stabilize the cation radicals while electron-withdrawing groups such as nitro group had the opposite effect.[14c] Therefore, it is possible to design electropolymerizable monomers by attaching two or more TPA units to an electron-withdrawing core.[15] Compared with the chemical routes, electrochemical polymerization can obtain polymer films on conductive substrates directly. This not only enlarges the scope of candidate polymers, but also avoids the procedure of the film coating. In this study, two TPA-terminated diamides **TPABP-DA** and **TPASO2-DA** and two TPA-terminated diimides **TPA6F-DI** and **TPASO2-DI** (**Scheme 2)** were synthesized and their electrochemistry and electropolymerization were investigated. It was found that the TPA-terminated diimides are more easily to undergo electropolymerization than the diamide analogs. The electrochemical and electrochromic properties of the electrogenerated films from the TPA-terminated diimides are also investigated. The experimental results suggested that the electrogenerated poly(amine-imide) films revealed reversible electrochemical redox reactions and obvious color changes upon electro-oxidation. This study provides new strategies for the easy fabrication of electroactive poly(amine-imide) films for electrochromic applications.



Scheme 1. Formation of radical cation and dimerization of triphenylamine (TPA).[14a]

Experimental part

Materials

4-Aminotriphenylamine (**TPA-NH2**) was synthesized by the cesium fluoride-mediated condensation of diphenylamine with *p*-fluoronitrobenzene, followed by a Pd/C-catalyzed hydrazine reduction.[16] Aniline (Acros), *p*-fluornitrobenzene (Acros), cesium fluoride (Acros), 10% palladium on charcoal (Pd/C, Fluka), triphenyl phosphite (TPP, Acros), and pyridine (Py, Wako) were used as received. *N,N*-Dimethylacetamide (DMAc, Fluka) and *N*-methyl-2-pyrrolidone (NMP, Tedia) were dried over calcium hydride for 24 h, distilled under reduced pressure, and stored over 4 Å molecular sieves in a sealed bottle. The aromatic dicarboxylic acids such as bis(4-carboxyphenyl) sulfone (New Japan

Chemicals Co.) and 4,4’-biphenydicarboxylic acid (TCI) were used as received. Commercially available tetracarboxylic dianhydrides such as 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA, Hoechst Celanese) and 3,4,3’,4’-diphenylsulfonetetracarboxylic dianhydride (DSDA, New Japan Chemical Co.) were heated at 250 ^{o}C in vacuo for 3 h before use. Tetrabutylammonium perchlorate (Bu_4NClO_4, Arcos) were recrystallized twice by ethyl acetate under nitrogen atmosphere and then dried *in vacuo* prior to use. All other reagents were used as received from commercial sources.

Instrumentation

Infrared (IR) spectra were recorded on a Horiba FT-720 FT-IR spectrometer. Elemental analyses were run in a Heraeus VarioEL III CHNS elemental analyzer. ^{1}H and spectra were measured on a Bruker AVANCE 500 FT-NMR system with tetramethylsilane as an internal standard. Electrochemical measurements were performed with a CH Instruments 750A electrochemical analyzer. The polymers were electropolymerized from 0.003 M monomers in dichloromethane (CH_2Cl_2) containing 0.1 M Bu_4NClO_4 as the electrolyte via repetitive cycling at a scan rate of 150 mV/s. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry was conducted with the use of a three-electrode cell in which ITO (polymer films area about 0.8 cm × 1.25 cm) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of a home-made Ag/AgCl, KCl (sat.) reference electrode. Ferrocene was used as an external reference for calibration (+0.48 V vs. Ag/AgCl). Spectroelectrochemistry analyses were carried out with an electrolytic cell, which was composed of a 1 cm cuvette, ITO as a working electrode, a platinum wire as an auxiliary electrode, and a Ag/AgCl reference electrode. Absorption spectra in the spectroelectrochemical experiments were measured with an Agilent 8453 UV-Visible spectrophotometer.

Monomer synthesis

Diimide compounds TPA6F-DI and TPASO2-DI. The diimide compounds **TPA6F-DI** and **TPASO2-DI** were prepared from the condensation reactions of **TPA-NH2** with 6FDA and DSDA, respectively. As a typical example, the synthetic procedure for **TPASO2-DI** is described as follows. A mixture of 2.60 g (10.0 mmol) of **TPA-NH2** and 1.79 g (5.0 mmol) dianhydride DSDA was dissolved in 15 mL of DMAc in a 50 mL round-bottom flask. The mixture was stirred 30 min at room temperature, then 4 mL of acetic anhydride and 2 mL of pyridine were added. The reaction mixture was further stirred for 1 h. The solution was poured slowly with stirring into 150 mL of methanol, and then the precipitated pale yellow product was collected by filtration, washed with water, and dried in vacuum at 80 ^{o}C to give 4.22 g (94% yield) of the desired monomer (**TPASO2-DI**) as yellow powder. Mp = 286 ^{o}C (DSC endotherm peak temperature), measured by DSC at 10 ^{o}C/min. IR (KBr) (Figure 1): 1780 cm^{-1} (asymmetric imide C=O stretching), 1722 cm^{-1} (symmetric imide C=O stretching). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm) (for the peak assignments, see Figure 2): 7.10 (t, J = 8.5 Hz, 4H, H$_a$), 7.16 (d, J = 9.0 Hz, 4H, H$_d$), 7.17 (d, J = 8.5 Hz, 8H, H$_c$), 7.23 (d, J = 9.0 Hz, 4H, H$_e$), 7.31 (t, J = 8.5 Hz, 8H, H$_b$), 8.16 (d, J = 8.0 Hz, 2H, H$_h$), 8.47 (dd, J = 8.0, 1.5 Hz, 2H, H$_g$), 8.53 (d, J = 1.5 Hz, 2H, H$_f$).

Diamide compounds TPABP-DA and TPASO2-DA. The diamide compounds **TPABP-DA** and **TPASO2-DA** were prepared from the condensation reactions of **TPA-NH2** with 4,4'-biphenyldicarboxylic acid and bis(4-carboxyphenyl) sulfone, respectively. As a typical example, the synthetic procedure for **TPASO2-DA** is described as follows. In a 50 mL round-bottom flask equipped with a stirring bar, a mixture of 2.10 g (10.0 mmol) of **TPA-NH2**, 1.53 g (5.0 mmol) of bis(4-carboxyphenyl) sulfone, 0.60 mL of triphenyl phosphite (TPP), 0.20 mL of pyridine, and 1 mL of NMP was heated with stirring at 120 °C for 3 h. The solution was poured into 150 mL of methanol to precipitate a white product. The precipitated product was collected by filtration, washed repeatedly with methanol and hot water, and dried in vacuum at 80 ^{o}C to give 3.56 g (90 % yield) of **TPASO2-DA** as off-white powder. Mp = 197 ^{o}C (DSC endotherm peak temperature), measured by DSC at 10 ^{o}C/min. IR (KBr) (Figure 1): 3303 cm^{-1} (amide N-H stretching), 1658 cm^{-1} (amide C=O stretching). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm) (for the peak assignments, see Figure 2): 7.00 (t, J = 7.5 Hz, 4H, H_a), 7.05 (d, J = 8.5 Hz, 4H, H_d), 7.06 (d, J = 7.5 Hz, 8H, H_c), 7.23 (t, J = 7.5 Hz, 8H, H_b), 7.49 (d, J = 8.5 Hz, 4H, H_e), 7.93 (d, J = 7.5 Hz, 4H, H_f), 7.96 (d, J = 7.5 Hz, 4H, H_g), 8.06 (s, 2H, amide).

Electrochemical polymerization

Electrochemical polymerization was performed with a CH Instruments 750A electrochemical analyzer. The polymers were synthesized from 0.003 M monomers in 0.1 M Bu_4NClO_4/CH_2Cl_2 solutions via cyclic voltammetry (CV) repetitive cycling at a scan rate of 150 mV/s. The polymer was deposited onto the surface of the working electrode surface (platinum disc or ITO/glass surface, polymer films area about 0.8 cm × 1.25 cm) were rinsed with plenty of acetone for the removal of inorganic salts and other organic impurities formed during the process. The electrodeposited polymer films with a thickness of about 1.5 μm were obtained after ten CV cycles between 0 V and 1.6 V or 1.8 V.

Fabrication of the electrochromic devices

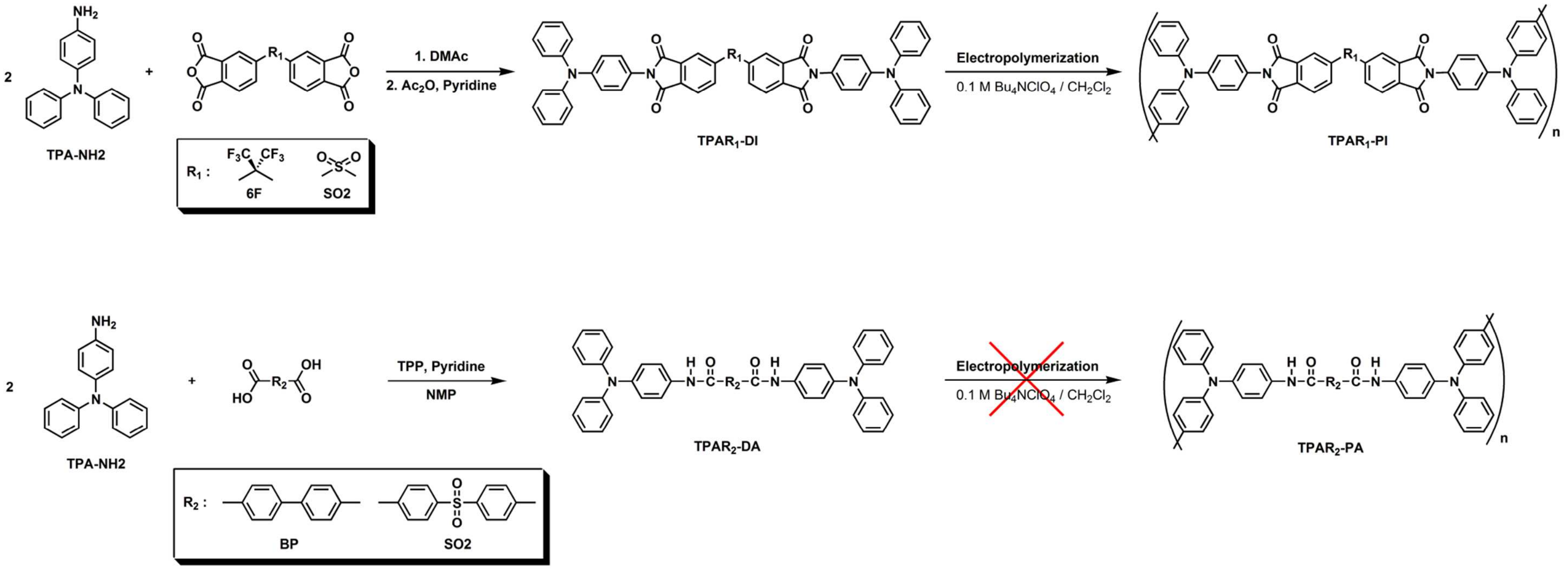
Electrochromic polymer films were prepared by electropolymerization of the **TPASO2-DI** onto an ITO-coated glass substrate (20 × 30 × 0.7 mm, 50-100 Ω/cm^{2}) by a method as described above. A gel electrolyte based on PMMA (Mw: 120000) and $LiClO_4$ was plasticized with propylene carbonate to form a highly transparent and conductive gel. PMMA (1 g) was dissolved in dry acetonitrile (4 mL), and $LiClO_4$ (0.1 g) was added to the polymer solution as supporting electrolyte. Then propylene carbonate (1.5 g) was added as plasticizer. The mixture was then gently heated until gelation. The gel electrolyte was spread on the polymer-coated side of the electrode, and the electrodes were sandwiched. Finally, an epoxy resin was used to seal the device.

Results and discussion

Monomer synthesis

The synthetic route and chemical structures of the TPA-terminated diamide and dimide compounds are shown in **Scheme 2**. **TPASO2-DA** and **TPABP-DA** were synthesized from 4-aminotriphenylamine (**TPA-NH2**) with bis(4-carboxyphenyl) sulfone and 4,4’-biphenydicarboxylic acid, respectively, using triphenyl phosphite (TPP) and pyridine as condensing agents. The diimide compounds **TPA6F-DI** and **TPASO2-DI** were prepared by the reactions of **TPA-NH2** with aromatic dianhydrides 6FDA and DSDA, respectively, followed by cyclodehydration with acetic anhydride and pyridine. IR and ^{1}H NMR spectroscopic techniques were used to identify structures of the target monomers.

Figure 1 shows the FT-IR spectra of **TPA-NH2** and all the synthesized monomers. The amino group of **TPA-NH2** showed the typical N-H stretching absorption pair at 3429 and 3350 cm^{-1}. After condensation with diacrboxylic acids or dianhydrides, the characteristic absorptions of the primary amino group disappeared. The IR spectra of **TPASO2-DA** and **TPABP-DA** showed the characteristic amide absorption bands at around 3300 cm^{-1} (N-H stretching) and 1650 cm^{-1} (amide carbonyl stretching). The characteristic imide absorption bands near 1780 cm^{-1} (asymmetric C=O stretching) and 1720 cm^{-1} (symmetric C=O stretching) could be observed in the IR spectra of **TPA6F-DI** and **TPASO2-DI**. **Figure 2** illustrates typical ^{1}H NMR spectra of **TPASO2-DA** and **TPASO2-DI**, and the spectra agree well with their proposed molecular structures.



Scheme 2. Synthesis and electropolymerization of the TPA-terminated diamide and dimide compounds.

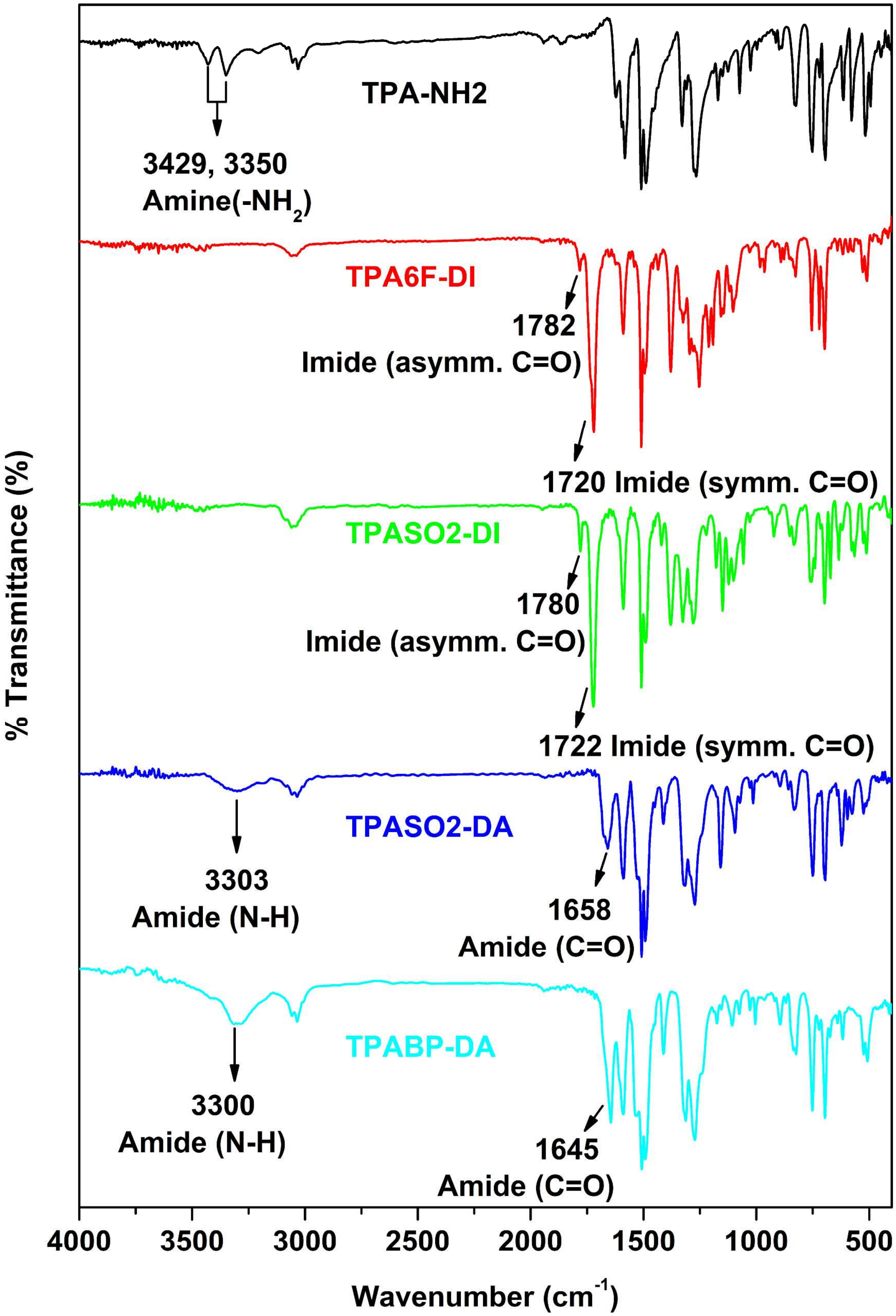


Figure 1. IR spectra of **TPA-NH$_2$** and all the synthesized monomers.

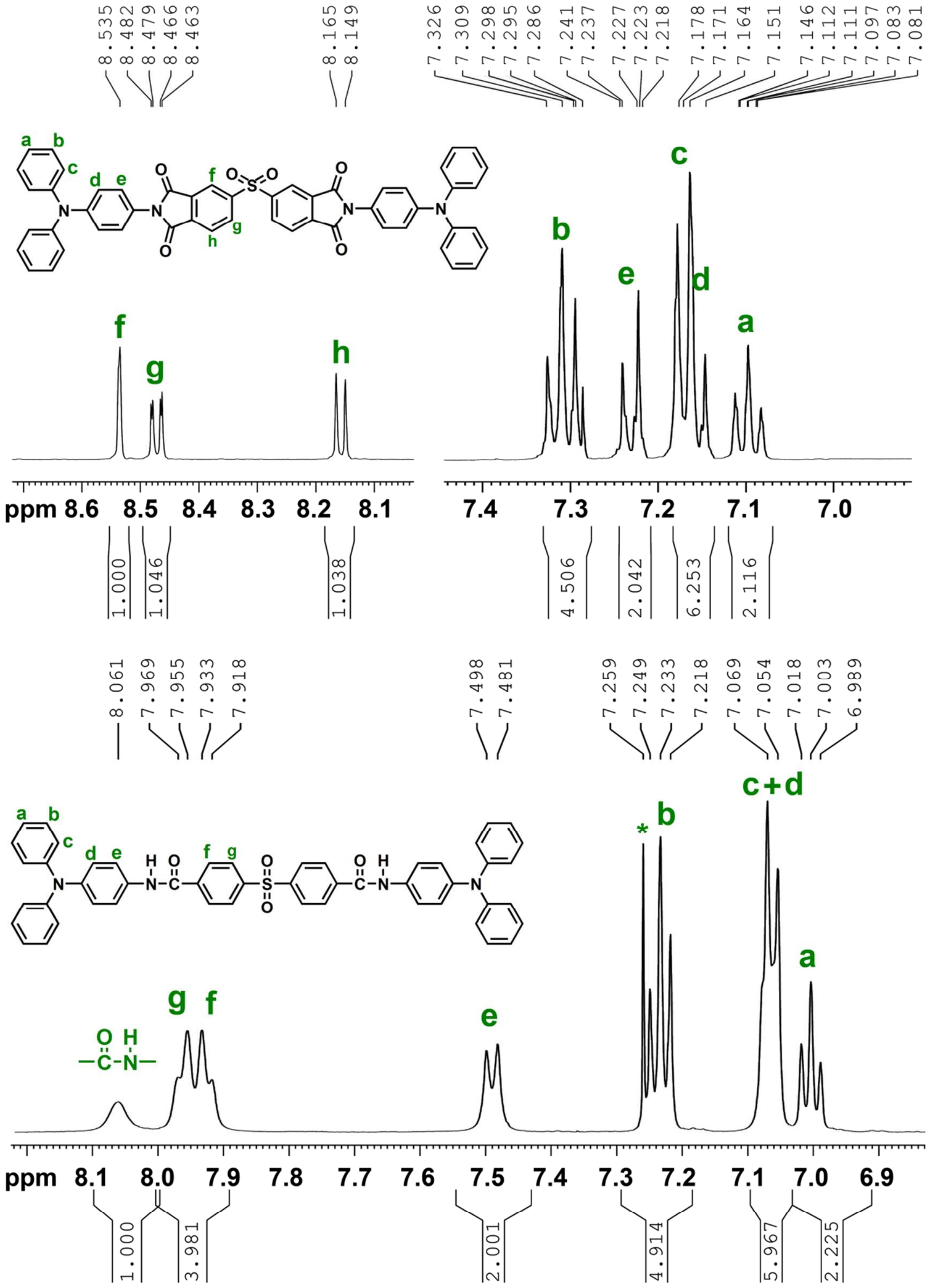


Figure 2. ^{1}H NMR spectra of **TPASO2-DI** and **TPASO2-DA** in $CDCl_3$. (*solvent peak)

Electrochemical properties of monomers

Figure 3 displays the successive cyclic voltammograms (CV) of 0.003 M **TPA6F-DI** and **TPASO2-DI** in 0.1 M Bu_4NClO_4/CH_2Cl_2 solutions between 0 and 1.8 V at a potential scan rate of 150 mV/s. As the CV scan continued, polymer film was formed on the working electrode surface. The increase in the redox wave current densities implied that the amount of conducting polymers deposited on the electrode was increasing. As shown in **Figure 3**, the polymerizations of **TPA6F-DI** showed two oxidation peaks, which are attributed to their polaronic and bipolaronic states, respectively. However, the two oxidation peaks of **TPASO2-DI** emerged to one broad peak after about five CV cycles.

For the first positive potential scan of **TPA6F-DI**, an oxidation peak at ca. 1.35 V was observed. From the first reverse negative potential scan, two cathodic peaks were detected. In the second scan, a new oxidation peak appeared at 1.01 V that was the complementary anodic process of the cathodic peak at a lower potential. The observation of a new oxidation couple in the second potential scan implies that the **TPA6F-DI** radical cations were involved in very fast electrochemical reactions that produced a substance that was easier to oxidize than was the parent **TPA6F-DI**. In addition, when the potential was continuously cycled, we observed a progressive growth in all peak currents. This behavior suggests that the oxidative coupling of the radical cations of **TPA6F-DI** produced a continuous build-up of an electroactive and conductive layer on the electrode.

In contrast, the electrochemical properties of the analogues **TPASO2-DA** and **TPABP-DA** are completely different. **Figure 4** displays their reversible electrochemical behavior, which indicates that the intermediates produced in the oxidation processes of these two compounds are stable on the time scale of the CV scan. Repetitive scans between 0 and 1.25 V produced almost the same patterns as those observed in the first scan, and no new peaks were detected under these experimental conditions. This reversible process suggests that the radical cations of the diamide compounds are more stable than those produced from the oxidation of the diimide analogues. Therefore, no polymer films were built on the electrode surface.

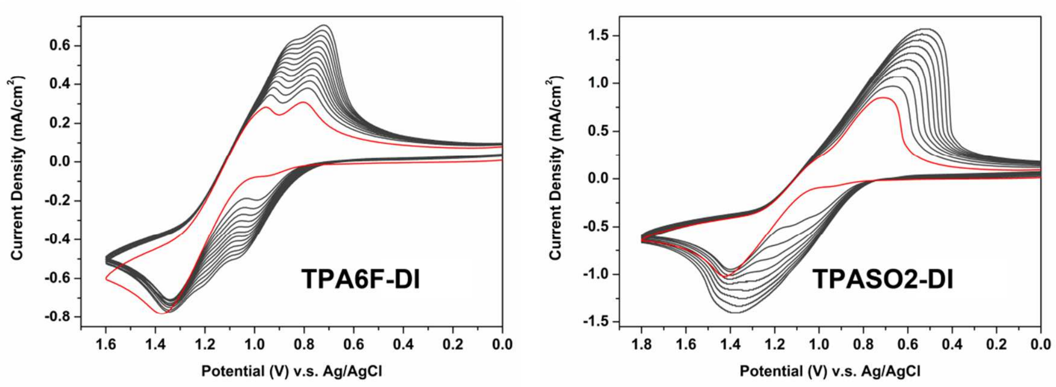


Figure 3. Repetitive cyclic voltammograms of 0.003 M **TPA6F-DI** and **TPASO2-DI** in 0.1 M Bu_4NClO_4/CH_2Cl_2 solutions at a scan rate of 150 mV/s. The first CV curves are marked in red.

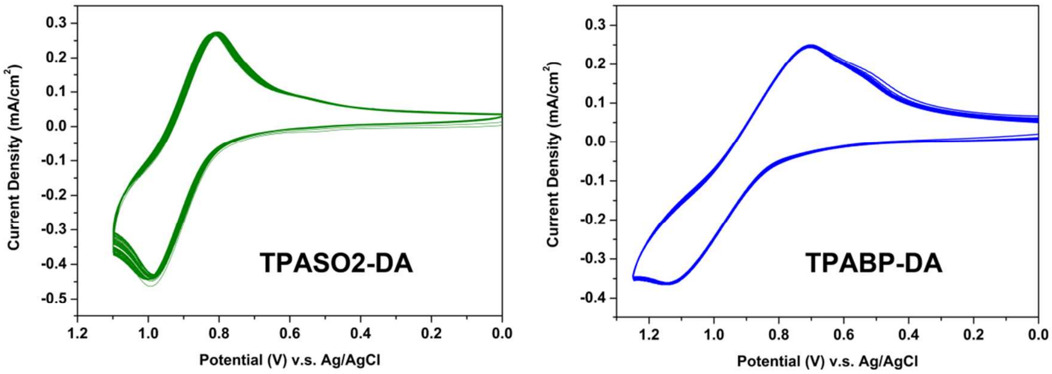


Figure 4. Repetitive cyclic voltammograms of 0.003 M **TPASO2-DA** and **TPABP-DA** in 0.1 M Bu_4NClO_4/CH_2Cl_2 solutions at a scan rate of 150 mV/s.

Electrochemical properties of the polymer films

The electrochemical behavior of the electrodeposited polymer films **TPA6F-DI** and **TPASO2-DI** was investigated by cyclic voltammetry in a monomer-free Bu_4NClO_4/CH_2Cl_2 solution. The quantitative details are summarized in **Table 1**. As shown in **Figure 5**, these two polymer films showed only one oxidation peak, although two oxidation processes of the TBP moiety were expected (**Scheme 3**). The half-wave potentials ($E_{1/2}$) of **TPA6F-PI** and **TPASO2-PI** were read at 0.96 V. Furthermore, irreversible reduction waves for the formation of radical anions and dianions of the imide units in **TPA6F-PI** and **TPASO2-PI** were observed in the negative side of the voltammograms at peak potentials $E_{pc} = -1.41$ and -1.54 V, respectively (**Figure 5**). The irreversible behavior may be caused by a little unwanted delamination or dissolution of the radical anion and dianion products in DMF/electrolyte solution. **Figure 6** shows the electrochemical behavior of the **TPASO2-PI** films at different scan rates between 50 and 500 mV/s in 0.1 M Bu_4NClO_4/CH_3CN. A linear dependence of the peak currents as a function of scan rates indicated that the electrochemical processes of these polymers are reversible and not diffusion limited. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the corresponding polymers were estimated from the $E_{1/2}^{ox}$ 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 levels for **TPA6F-PI** and **TPASO2-PI** were calculated to be 5.32 eV (relative to the vacuum energy level), whereas the values for the LUMO levels lay at about 2.28 - 2.32 eV.

Table 1 Optical and electrochemical properties of the polymer films.

Polymer	UV–vis absorption (nm)[a]		Oxidation potential (V)[b]		Reduction potential (V)[c]	E_g (eV)[d]	HOMO (eV)[e]	LUMO (eV)[e]
	λ_{max}	λ_{onset}	E_{onset}	$E_{1/2}^{Ox}$	$E_{1/2}^{Red}$			
TPA6F-PI	354	408	0.76	0.96	−1.18	3.04	5.32	2.28
TPASO2-PI	347	414	0.81	0.96	−0.97	3.00	5.32	2.32

[a] UV-vis absorption wavelengths of the polymer thin films.

[b] Calculated from first CV scans, versus Ag/AgCl in acetonitrile at a scan rate of 50 mV/s.

[c] Calculated from first CV scans, versus Ag/AgCl in DMF at a scan rate of 50 mV/s.

[d] Optical bandgaps calculated from absorption edge of the polymer films: $E_g = 1240/\lambda_{onset}$.

[e] $E_{HOMO} = -(E_{1/2}^{Ox1} + 4.8)$ (eV); $E_{LUMO} = E_{HOMO} - E_g$.

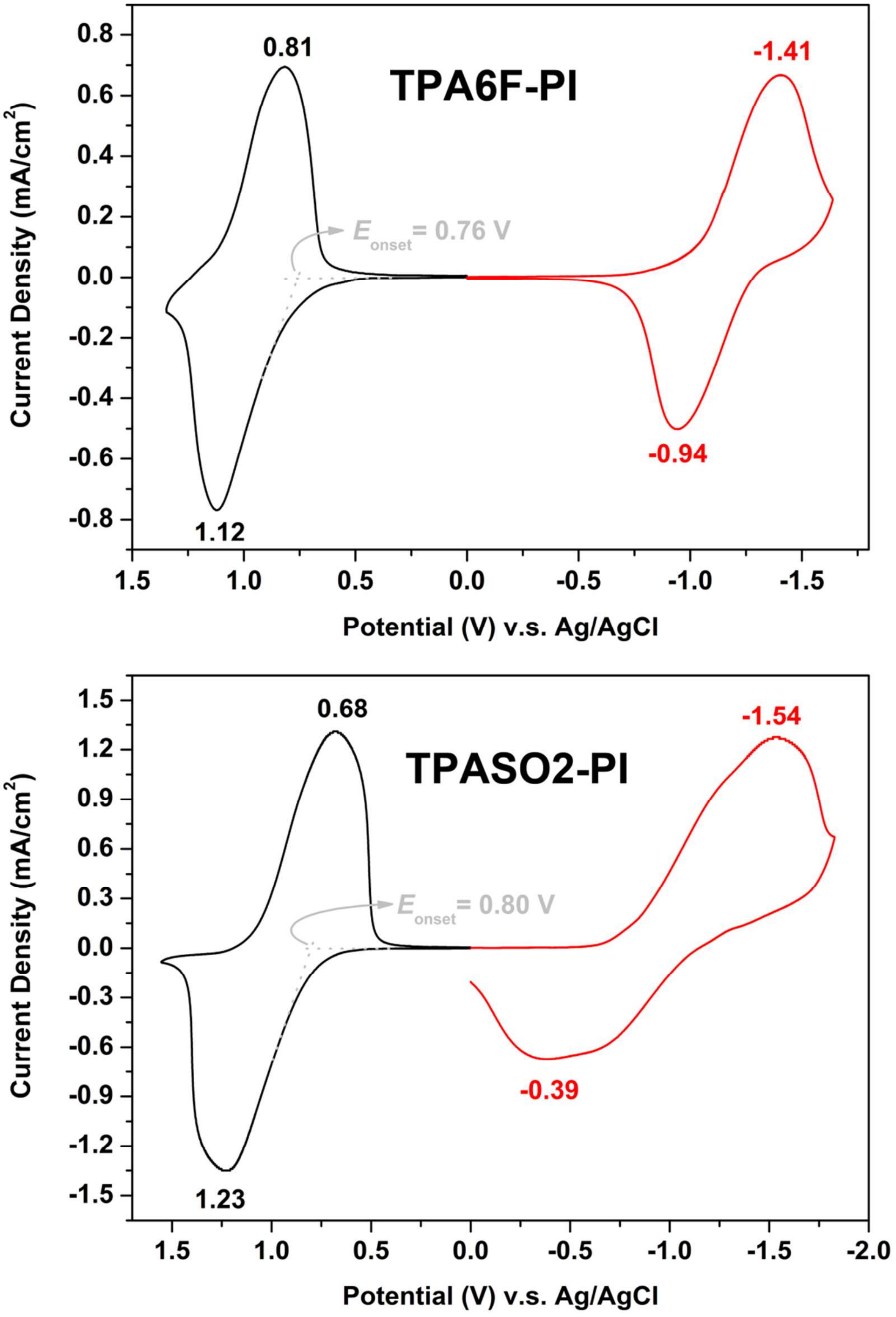
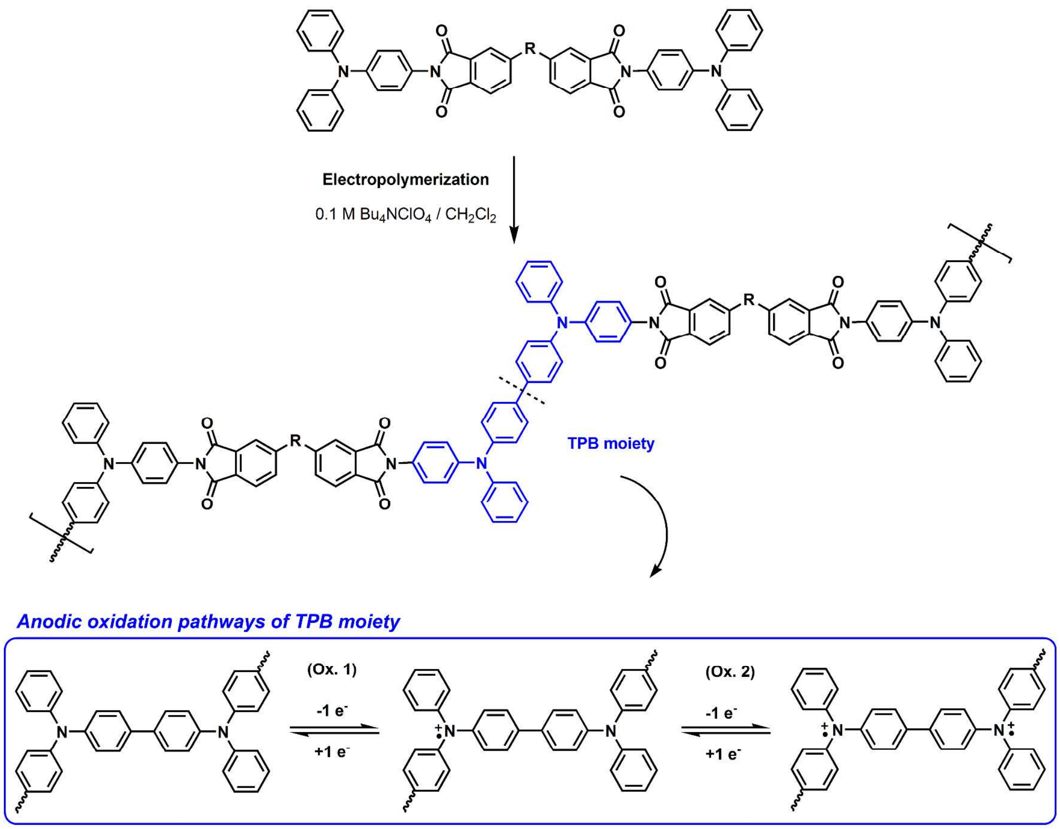


Figure 5. Cyclic voltammograms of the polymer films on the ITO-coated glass slide in 0.1 M Bu_4NClO_4/CH_3CN (for anodic process) and DMF (for cathodic process) at a scan rate of 50 mV/s.



Scheme 3. Electropolymerization and anodic oxidation pathways of the TPB unit.

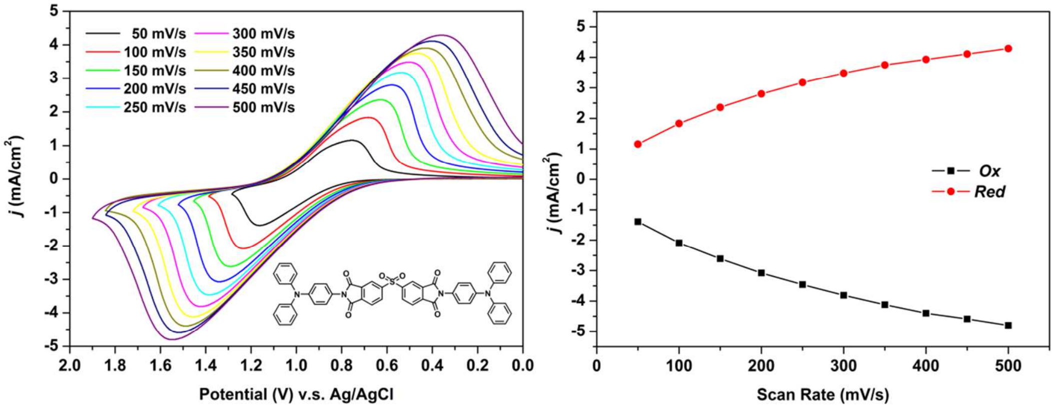


Figure 7. Scan rate dependence of the **TPASO2-PI** film on the ITO-coated glass slide in CH_3CN containing 0.1 M Bu_4NClO_4 at different scan rates between 50 and 500 mV/s.

Spectroelectrochemical and electrochromic properties

Spectroelectrochemistry were performed on the electrogenerated polymeric films on ITO glass to clarify its electronic structure and optical behavior upon oxidation. The typical UV-vis-NIR absorption spectra and electrochromic behavior of **TPASO2-PI** at various applied potentials are illustrated in **Figure 7**. In the neutral state, polymer **TPASO2-PI** exhibited strong absorption at wavelength around 354 nm, characteristic for triarylamine π-π* transitions, but it was almost transparent in the visible region. When the applied potential was gradually raised from 0.0 to 1.2 V, the absorption intensity at 354 nm slightly dropped and two new bands appeared at 487 nm and 724 nm accompanied with a broad band having its maximum around 1100 nm in the NIR region. We attribute this spectral change to the formation of a stable monocation radical from the tetraphenylbenzidine (TPB) moiety. When the applied potential was set at 1.3 V, a strong absorption band at around 720 nm was observed, whereas the absorption peak at 354 nm and 487 nm decreased gradually in intensity. This absorption change indicated the formation of a stable dicationic speicies from the TPB moiety. The observed electronic absorption changes in the film of polymers at various potentials are fully reversible and are associated with strong color change; indeed, they even can be seen readily by the naked eye. Its color changes from pale yellowish (neutral state) to orange (semi-oxidized state) and blue (fully oxidized state).

The stability of the oxidized species towards repetitive switching was assessed from the transmittance percent variation with applied potentials. The polymer film was potential stepped between its neutral (0 V) and the oxidized state at +1.2 V and +1.3 V, respectively, with a residence time of 9 s. While the films were switched, the absorbance at 487 nm and 724 nm was monitored as a function of time with UV-vis-NIR spectroscopy. Switching data for the electrogenerated film of **TPASO2-PI** are given in **Figure 8**. The switching time was calculated at 90% of the full switch because it is difficult to perceive any further color change with naked eye beyond this point. As shown in **Figures 8a** and **8b**, after over 20 cyclic scans between 0 V and 1.2 V or between 0 V and 1.3 V, the polymer films still exhibited good reversibility of electrochromic characteristics. When the applied voltage was stepped between 0 and 1.2 V, the **TPASO2-PI** film exhibited high contrast of optical transmittance change (ΔT%) up to 42 % at 487 nm for orange coloring and required 3.7 s for switching absorbance and 0.8 s for bleaching (**Figure 8c**). When the applied voltage was stepped between 0 and 1.3 V, the **TPASO2-PI** film exhibited ΔT% up to 84 % at 724 nm for blue coloring and required 3.1 s for the coloring process and 1.3 s for the bleaching process (**Figure 8d**). The electrochromic coloring efficiency (CE) of orange ($\eta = \Delta OD_{487}/Q$) and sky blue coloring ($\eta = \Delta OD_{724}/Q$) of the **TPASO2-PI** film was calculated to be 251 cm^2/C and 150 cm^2/C, respectively (**Table 2**). Therefore, all these results revealed that this electrochemically generated film exhibits high redox stability and good electrochromic performance.

Based on previous results, it can be concluded that these polymers can be used in the construction of electrochromic devices and optical display. The polymer films were electrodeposited onto ITO-coated glass and then dried. Afterward, the gel electrolyte was spread on the polymer-deposited side of the electrode and the electrodes were sandwiched under atmospheric condition. To prevent leakage, an epoxy resin was applied to seal the device. As a typical example, an electrochromic device based on polymer **TPASO2-PI** was fabricated. The spectral and color changes of the electrochromic device of polymer **TPASO2-PI** upon oxidation are illustrated in **Figure 9.** By the application of voltage to 1.9 V, the absorption bands at 487 and 717 nm gradually increased in intensity. Upon further oxidation at applied voltages to 2.1 V, a broadband at about 717 nm grew up continuously. When the voltage applied was increased (to a maximum of 2.4 V), the color changed from colorless (neutral) to orange (semi-oxidized) and blue (fully oxidized).

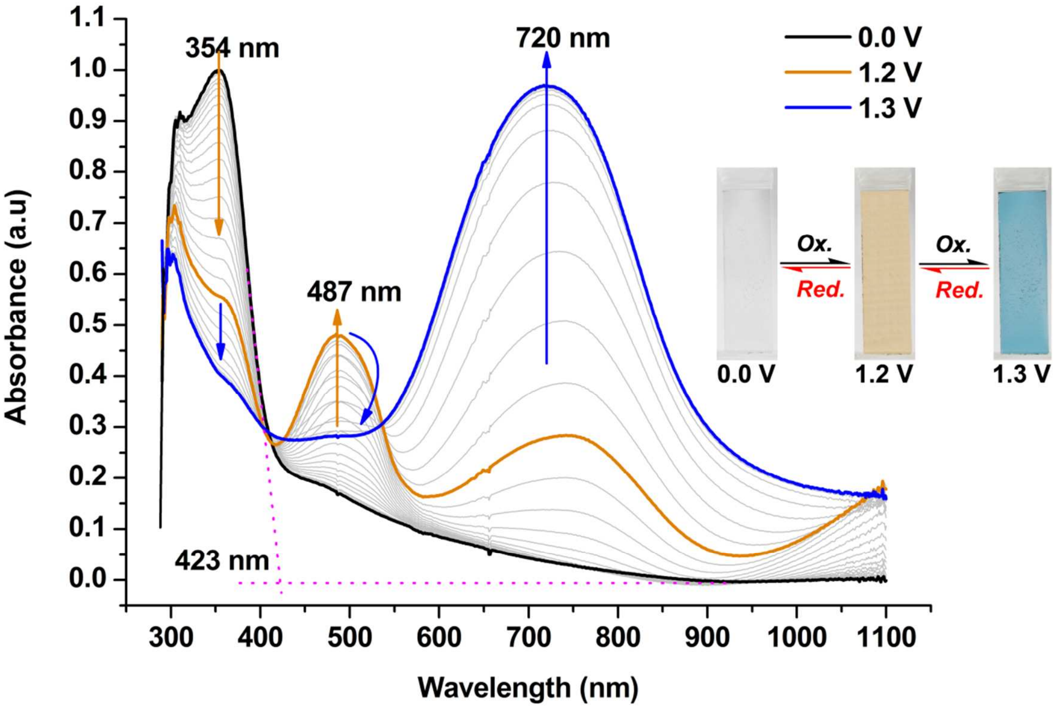


Figure 7. Spectroelectrochemistry and color changes of the **TPASO2-PI** film on an ITO-coated glass in 0.1 M Bu_4NClO_4/CH_3CN at various applied potentials (v.s. Ag/AgCl).

Table 2 Electrochromic properties of the **TPASO2-PI** film.

Polymer	λ_{max}[a] (nm)	Δ%T	Response time[b]		ΔOD[c]	Q_d[d] (mC/cm^2)	CE[e] (cm^2/C)
			t_c (s)	t_b (s)			
TPASO2-PI	487	42	3.7	0.8	0.336	1.34	251
	724	84	3.1	1.3	0.763	5.10	150

[a] Wavelength of absorption maximum.

[b] Time for 90% of the full-transmittance change.

[c] Optical Density (ΔOD) = $\log[T_{bleached}/T_{colored}]$, where $T_{colored}$ and $T_{bleached}$ are the maximum transmittance in the oxidized and neutral states, respectively.

[d] Q_d is ejected charge, determined from the *in situ* experiments.

[e] Coloration efficiency (CE) = ΔOD/Q_d

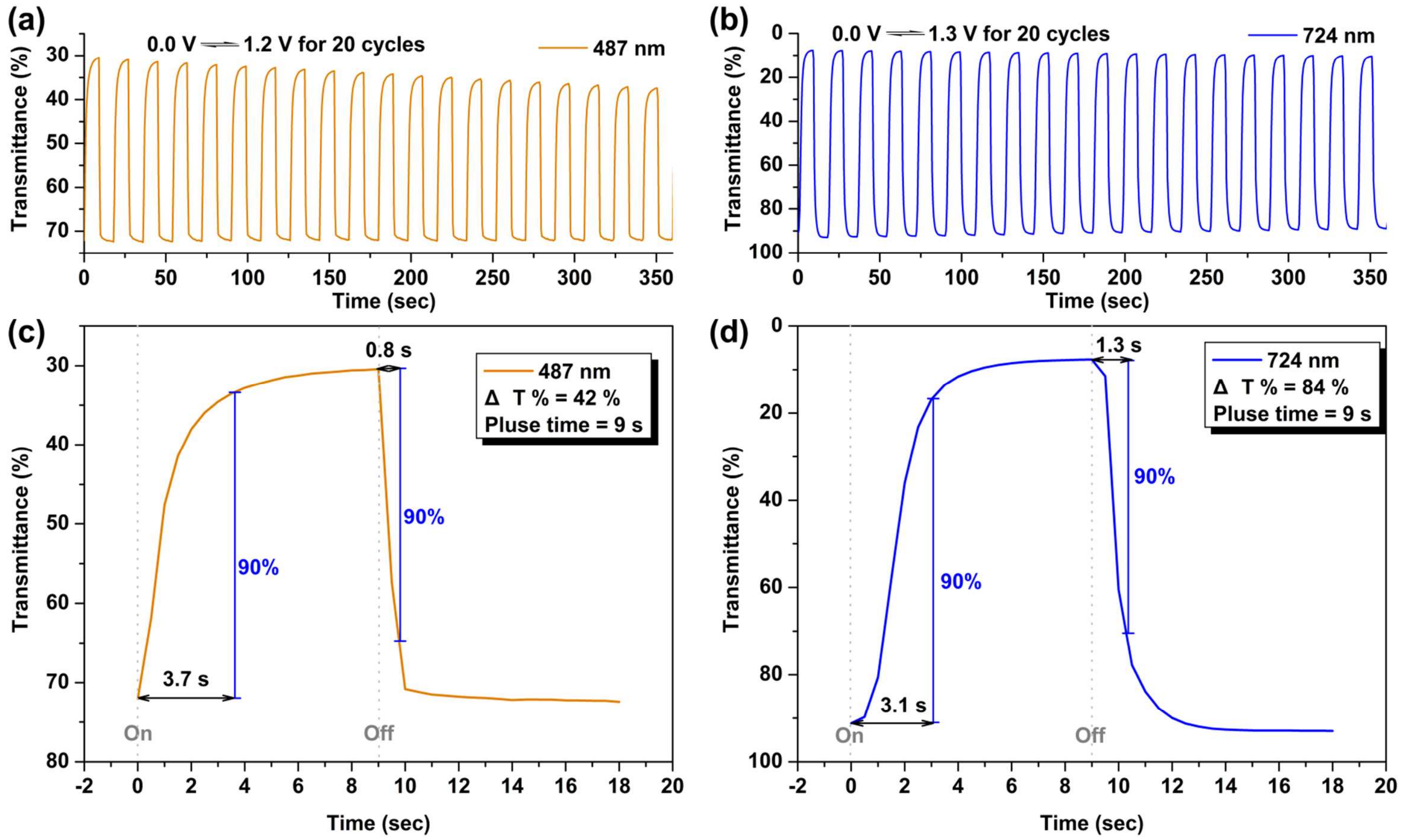


Figure 8. Optical transmittance changes for polymer **TPASO2-PI** on the ITO-glass slide in 0.1 M Bu_4NClO_4/CH_3CN while the potential was switched (a) between 0.0 V and 1.2 V at 487 nm and (b) between 0.0 V and 1.3 V at 724 nm with a pulse time of 9 s. Calculation of optical switching time at (c) 487 nm and (d) 724 nm.

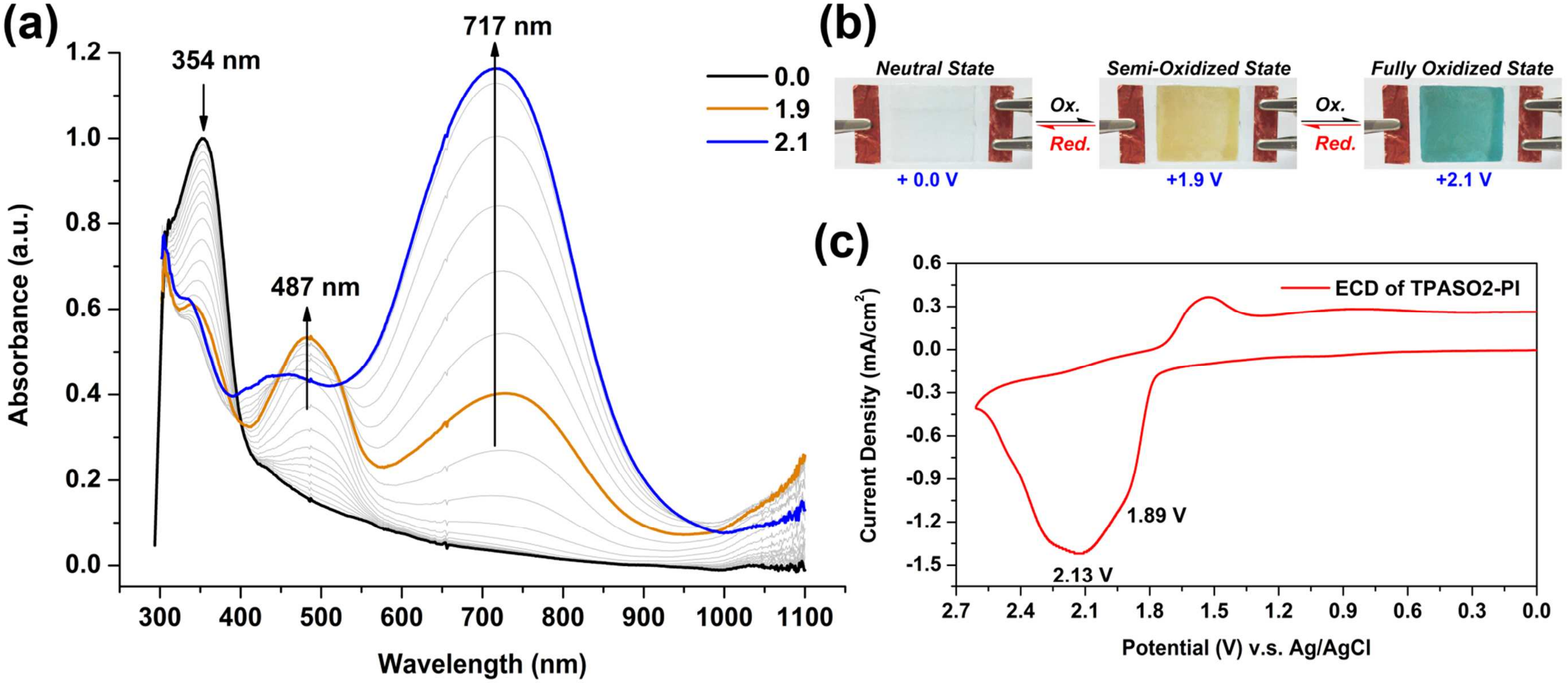


Figure 9. (a) Spectroelectrochemistry of the device**,** (b) photos of sandwich-type ITO-coated glass electrochromic cell, and (c) cyclic voltammograms of the polymer film in the electrochromic device based on **TPASO2-PI**.

Conclusions

Two series of novel TPA-endcapped aromatic diamide and diimide monomerss were synthesized from the condensation of 4-aminotriphenylamine with dicarboxylic acids and tetracarboxylic dianhydrides, respectively. Polymer films with tetraphenylbenzidine (TPB) segments were successfully electrodeposited onto the ITO electrode surface by electropolymerization of the diimide compounds in Bu_4NClO_4/CH_2Cl_2. However, no polymer films were built on the electrode surface using the diamide analogues. The resulting polymer films of the diimide compounds exhibited reversible oxidation redox couples due to oxidations of the TPB unit. The electrogenerated polymer films also revealed high electrochemical and electrochromic stability, with coloration change from a colorless neutral state to orange and sky blue oxidized forms. Thus, these film materials formed by the electrochemical polymerization of TPA-containing diimide monomers present a new entry to the polymeric electrochromics that may find potential application in the fabrication of electrochromic devices.

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