Supplementary Information (SI) for Journal of Materials Chemistry C.

Supplementary Information

Electrochemical and electrochromic properties of aromatic polyamides and polyimides with phenothiazine-based multiple triphenylamine cores

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Experimental section

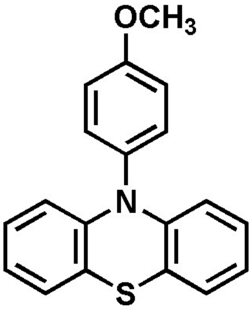
Monomers Synthesis

Materials

Phenothiazine (Acros), *p*-fluoronitrobenzene (Acros), 4-iodoanisole (Acros), potassium carbonate (K_2CO_3, Showa), Copper(I) iodide (CuI, Acros), *N*-Bromosuccinimide (NBS, Alfa Aesar), *p*-Anisidine (TCI), triethylamine (Acros), Triethylene glycol dimethyl ether (TEGDME, Acros), Tetrahydrofuran (THF, Tedia), 99% hydrazine monohydrate (TCI), 10% palladium on activated carbon (Pd/C, Fluka), and triphenyl phosphite (TPP, TCI) were used without further purification. *N,N*-dimethylacetamide (DMAc), pyridine (Py, Wako), and *N*-methyl-2-pyrrolidone (NMP, Tedia) was dried over calcium hydride for 24 h, distilled under reduced pressure, and stored over 4 Å molecular sieves in sealed bottles. Commercially obtained calcium chloride ($CaCl_2$) was dried under vacuum at 180 °C for 3 h prior to use. Tetrabutylammonium perchlorate (TBAP; Bu_4NClO_4, TCI) was recrystallized from ethyl acetate under nitrogen atmosphere and then dried in vacuum prior to use. All other reagents and solvents were used as received from commercial sources. The aromatic dicarboxylic acid monomers such as 2,2-bis(4-carboxyphenyl)hexafluoropropane (**5a**, TCI) and 4,4'-dicarboxydiphenyl ether (**5b**) (TCI) were used as received from commercial sources. The aromatic tetracarboxylic dianhydrides including 4,4'-(hexafluoroisopropylidene)diphthalic dianhydride (**7a**, 6FDA) (Hoechst Celanese) and 4,4'-oxydiphthalic dianhydride (**7b**, ODPA) (Oxychem) were dried at 250 °C in vacuo for 3 h. According to a well-established synthetic procedure [Ref. **S1**], the 1,4-Bis(4-carboxyphenoxy)benzene (**5c**) (mp = 322–324°C) was synthesized by alkaline hydrolysis of 1,4-bis(4-cyanophenoxy)benzene resulting from the condensation of 1,4-dihydroxybenzene with *p*-fluorobenzonitrile in the presence of potassium carbonate. 1,4-Bis(3,4-dicarboxyphenoxy)benzene dianhydride (**7c**) was synthesized according to a previously reported method [Ref. **S2**]. 4-Methoxy-4'-nitrodiphenylamine, was prepared on the basic of a well-known chemistry [Ref. **S3**].

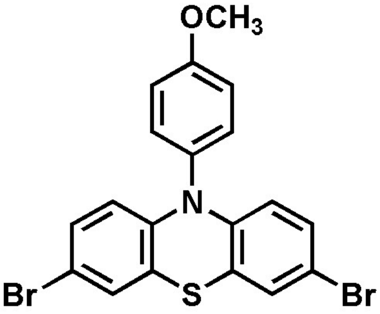
10-(4-Methoxyphenyl)phenothiazine (1)

In a 250-mL three-necked round bottom flask equipped with a stirring bar, 10.0 g (0.05 mol) of phenothiazine, 3.81 g (0.02 mol) of Copper(I) iodide, 14.0 g (0.06 mol) of 4-iodoanisole and 27.6 g (0.2 mol) of potassium carbonate were dissolved in 20 mL of TEGDME under nitrogen atmosphere. The mixture was heated at 180 °C and held at that temperature for 24 h. The inorganic salts were removed by filtration of the hot reaction mixture. Then the filtrate was slowly poured into 100 mL of stirred methanol, and the precipitated product was collected by filtration, washed with methanol, and recrystallized from ethyl acetate to afford 9.77 g (64 % yield) of green crystals with melting point of 174−176 °C (by DSC) (lit. [Ref. **S4**] 176−177°C). FT-IR (KBr): 2950, 2827 cm^{-1} (−OCH_3 C−H stretch).



3,7-Dibromo-10-(4-methoxyphenyl)phenothiazine (2)

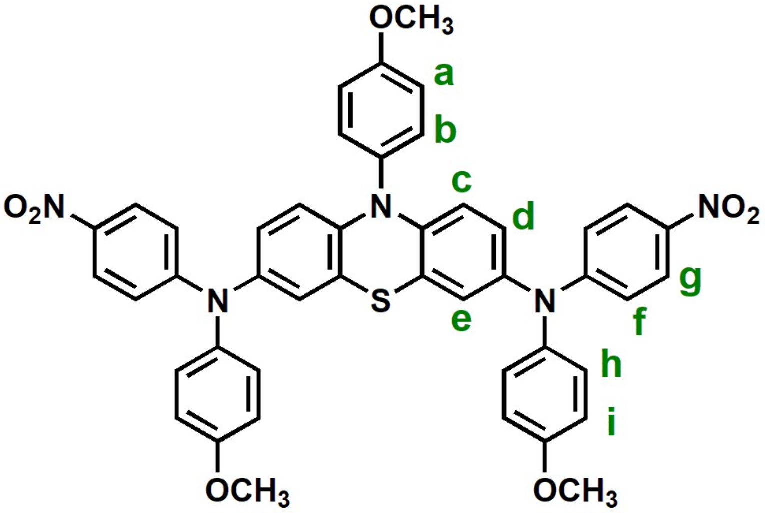
In a 100-mL three-necked round bottom flask equipped with a stirring bar, 1.83 g (6 mmol) of compound **1** was dissolved in 30 mL of THF under nitrogen atmosphere. Cool the reaction to 0 ºC and slowly add 2.67 g of NBS (15 mmol) that dissolved in 20 mL of THF in advance. The mixture was step by step to room temperature and held at room temperature for 24 h. Add 50 ml of distilled water to form an emulsion and evaporate THF. Recrystallize the crude mixture from ethanol to afford 2.45 g (88 % yield) of yellowish powder with melting point of 156−158 °C (by DSC) (lit. [Ref. S5] 157−158°C). FT-IR (KBr): 2950, 2827 cm^{-1} (−OCH_3 C−H stretch).



3,7-Bis[(4-nitrophenyl)(4'-methoxyphenyl)amino]-10-(4-methoxyphenyl)-phenothiazine (3)

In a 250-mL three-necked round bottom flask equipped with a stirring bar, 2.78 g (6 mmol) of **2**, 0.95 g (5 mmol) of Copper(I) iodide, 4.40 g (18 mmol) of 4-Methoxy-4'-nitrodiphenylamine and 6.63 g (48 mmol) of potassium carbonate were dissolved in 20 mL of TEGDME under nitrogen atmosphere. The mixture was heated at 180 ^{o}C and held at that temperature for 48 h. The inorganic salts were removed by filtration of the hot reaction mixture. Then the filtrate was slowly poured into 100 mL of stirred methanol, and the precipitated product was collected by filtration and purify the product by flash chromatography on silica gel (dichloromethane/hexane 3:1). The product recrystallized from acetone to afford 1.66 g (35 % yield) of dark red crystals with a melting point of 226−228 °C (by DSC).

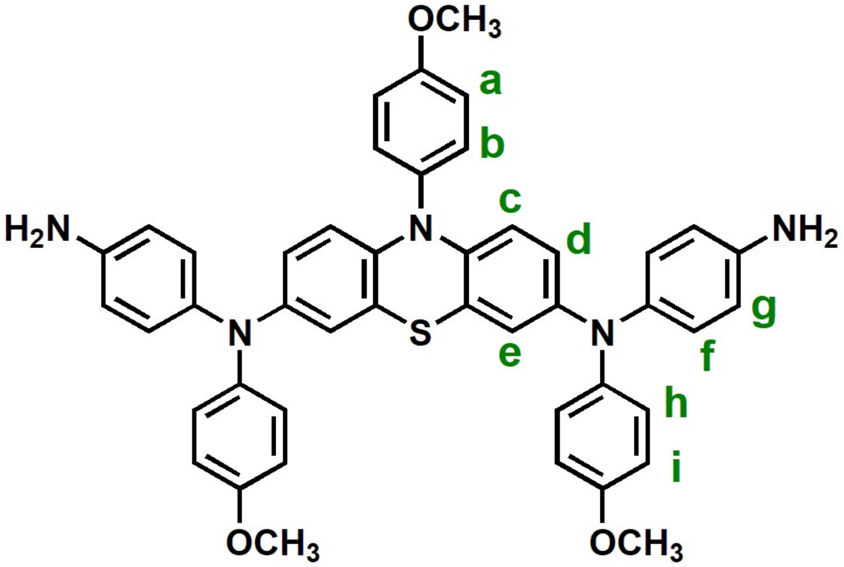
FT-IR (KBr): 2950, 2827 cm^{-1} (−OCH_3 C−H stretch), 1586, 1312 cm^{-1} (−NO_2 stretch). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 3.77 (s, 6H, −OCH_3), 3.84 (s, 3H, −OCH_3), 6.19 (d, *J* = 8.8 Hz, 2H, H_c), 6.66 (d, *J* = 7.3 Hz, 4H, H_f), 6.90 (d, *J* = 8.8 Hz, 2H, H_d), 6.99-7.01 (m, 6H, $H_e + H_i$), 7.19-7.23 (m, 6H, $H_a + H_h$), 7.40 (d, 2H, H_b), 8.01 (d, *J* = 7.3 Hz, 4H, H_g).



3,7-Bis[(4-aminophenyl)(4-methoxyphenyl)amino]-10-(4-methoxyphenyl)-phenothiazine (4)

In a 250 mL three-neck round-bottom flask equipped with a stirring bar, 1.18 g (1.5 mmol) of dinitro compound **3** and 0.10 g of 10 % Pd/C were dissolved/suspended in 75 mL of ethanol and 25 mL of THF under nitrogen atmosphere. The suspension solution was heated to reflux, and 1.5 mL of hydrazine monohydrate was added slowly to the mixture. After a further 24 h of reflux, the solution was filtered hot to remove Pd/C, and the filtrate was cooled to precipitate white powder. The product was collected by filtration and dried in vacuum at 50 °C to give 0.94 g (86% yield) of yellow-green powder.

FT-IR (KBr): 3468, 3375 cm^{-1} (−NH_2 stretch), 2950, 2827 cm^{-1} (−OCH_3 C−H stretch). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 3.68 (s, 6H, −OCH_3), 3.81 (s, 3H, −OCH_3), 4.95 (s, 4H, −NH_2), 6.06 (d, J = 6.2 Hz, 2H, H_c), 6.40-6.42 (m, 4H, H_d + H_e), 6.50 (d, J = 6.6 Hz, 4H, H_i), 6.70 (d, J = 6.7 Hz, 4H, H_h), 6.79 (d, J = 6.6 Hz, 4H, H_g), 6.83 (d, J = 6.7 Hz, 4H, H_f), 7.12 (d, J = 6.7 Hz, 2H, H_a), 7.28 (d, J = 6.7 Hz, 2H, H_b).

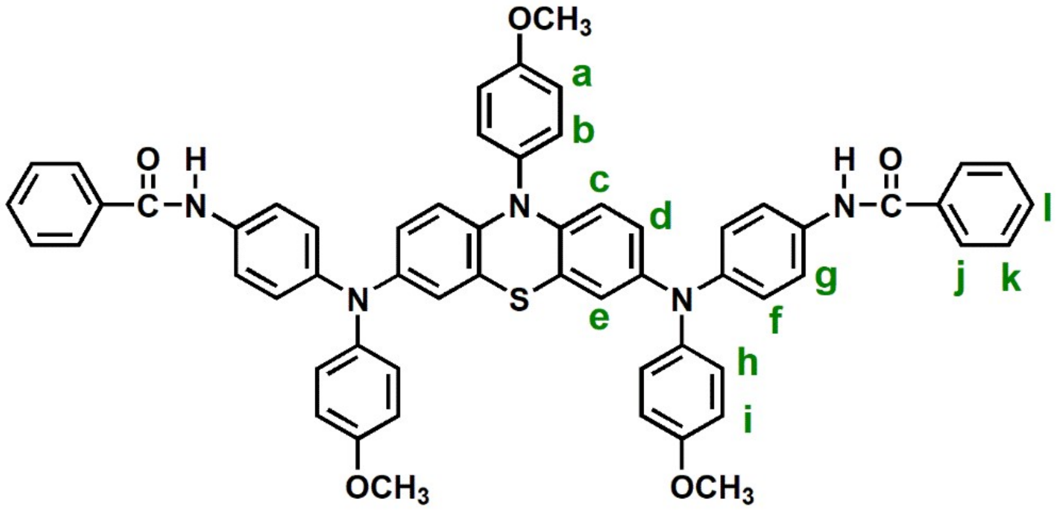


Synthesis of Model Compound

3,7-Bis-[(4-benzamidophenyl)(4-methoxyphenyl)amino]-10-(4-methoxyphenyl)-phenothiazine (M1)

In a 25-mL round bottom flask equipped with a stirring bar, a mixture of 0.29 g (0.4 mmol) of diamine **4**, 0.11 g (0.9 mmol) of benzoic acid, 0.10 g of anhydrous calcium chloride, 0.6 mL of triphenyl phosphite (TPP), 0.15 mL of pyridine, and 1 mL of NMP was heated at 120 °C for 3 h. The resulting solution was poured with stirring into methanol/H_2O. The precipitated product was washed repeatedly with methanol and hot water, and dried to give 0.30 g (81% yield) green powder of model compound **M1**.

FT-IR (KBr): 3294 cm^{-1} (amide N−H stretch), 2934, 2826 cm^{-1} (−OCH_3 C−H stretch), 1649 cm^{-1} (amide C=O stretch). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 3.72 (s, 6H, −OCH_3), 3.82 (s, 3H, −OCH_3), 6.12 (d, J = 9.5 Hz, 2H, H_c), 6.59 (m, 4H, H_d + H_e), 6.87 (m, 8H, H_i + H_f), 6.95 (d, J = 8.8 Hz, 4H, H_h), 7.17 (d, J = 8.8 Hz, 2H, H_a), 7.36 (d, J = 8.7 Hz, 2H, H_b), 7.51 (t, J = 7.2 Hz, 4H, H_k), 7.57 (t, J = 7.3 Hz, 2H, H_l), 7.62 (d, J = 8.9 Hz, 4H, H_g), 7.92 (d, J = 7.1 Hz, 4H, H_j) , 10.14 (s, 2H, amide N−H).

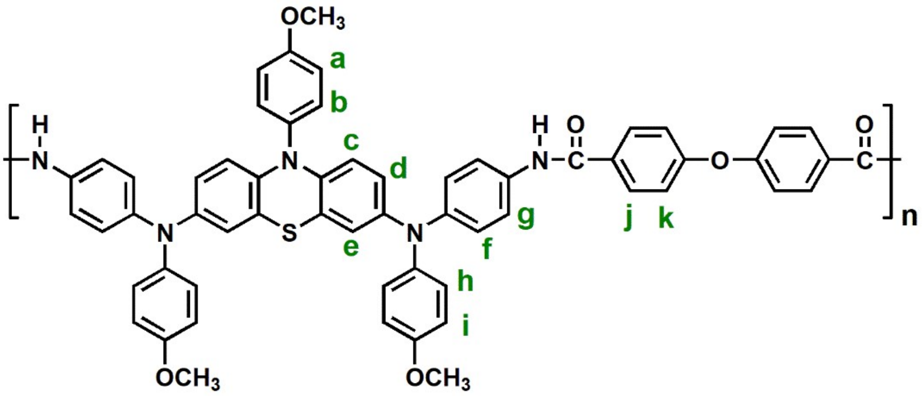


Polymer Synthesis

Synthesis of Polyamides

The synthesis of polyamide **6b** was used as an example to illustrate the general synthetic procedure used to produce the polyamides. A mixture of 0.44 g (0.6 mmol) of diamine monomer **4**, 0.15 g (0.6 mmol) of 4,4′-dicarboxydiphenyl ether (**5b**), 0.10 g of anhydrous calcium chloride, 0.6 mL of triphenyl phosphite (TPP), 0.15 mL of pyridine, and 1 mL of NMP was heated at 110 °C for 3 h. The polymerization proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solution. The resulting viscous solution was poured slowly with stirring into 100 mL of methanol, giving rise to a fibrous precipitate. The precipitated product was collected by filtration, washed repeatedly with methanol and hot water, and dried to give a quantitative yield of polyamide **6b**. The inherent viscosity of **6b** was 0.17 dL/g, measured in DMAc (containing 5 wt % LiCl) at a concentration of 0.5 g/dL at 30 ^{o}C.

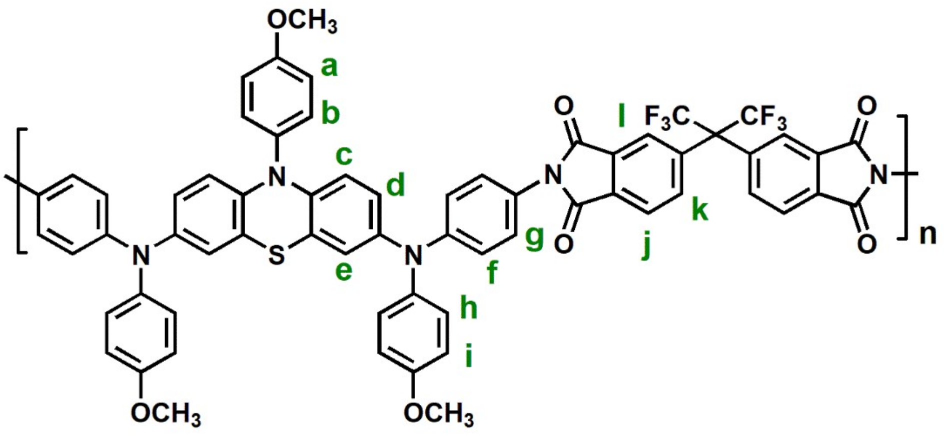
FT-IR (KBr): 3353 cm^{-1} (amide N−H stretch), 2934, 2826 cm^{-1} (−OCH_3 C−H stretch), 1637 cm^{-1} (amide C=O stretch). ^{1}H NMR (600 MHz, DMSO-d_6, δ, ppm): 3.72 (s, 6H, −OCH_3), 3.82 (s, 3H, −OCH_3), 6.09 (d, 2H, H_c), 6.58 (m, 4H, $H_d + H_e$), 6.85-6.93 (m, 12H, $H_h + H_i + H_f$), 7.16-7.21 (m, 6H, $H_a + H_k$), 7.34 (d, 2H, H_b), 7.60 (d, 4H, H_g), 8.00 (d, 4H, H_j), 10.12 (s, 2H, amide N−H).



Synthesis of Polyimides

The synthesis of polyimide **8a** is described as follow. The diamine monomer **4** (0.62 g, 0.85 mmol) was dissolved in 9.5 mL of dried DMAc in a 50 mL round bottom flask, followed by the addition of 6FDA (**7a,** 0.38 g, 0.85 mmol). Thus, the solid content of the solution is approximately 10 wt %. The mixture was stirred at room temperature for about 18 h to yield a viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) was 0.30 dL/g, measured in DMAc at a concentration of 0.5 g/dL at 30 ^{o}C. The poly(amic acid) film was obtained by casting from the reaction polymer solution onto a glass Petri dish and drying at 90 ^{o}C overnight. The poly(amic acid) in the form of solid film was converted to the polyimide film by successive heating at 150 ^{o}C for 1 h, 200 ^{o}C for 1 h, and 250 ^{o}C for 1 h. The inherent viscosity of polymer was 0.20 dL/g, measured in DMAc (containing 5 wt % LiCl) at a concentration of 0.5 g/dL at 30 ^{o}C.

FT-IR (KBr): 2934, 2826 cm^{-1} ($-OCH_3$ C−H stretch), 1783 cm^{-1} (asymmetrical imide C=O stretch), 1716 cm^{-1} (symmetrical imide C=O stretch). ^{1}H NMR (600 MHz, DMSO-*d*$_6$, δ, ppm): 3.67-3.74 (s, 6H, $-OCH_3$), 3.82 (s, 3H, $-OCH_3$), 6.13 (d, 2H, H_c), 6.61-6.72 (m, 4H, $H_d + H_e$), 6.72-6.80 (m, 6H, $H_a + H_f$), 6.83-6.96 (d, 4H, H_i), 7.04-7.10 (d, 4H, H_d), 7.15-7.18 (m, 6H, $H_g + H_b$), 7.69 (s, 2H, H_l), 7.91 (s, 2H, H_k), 8.10 (s, 2H, H_j).



Preparation of the Polymer Films

A polymer solution was made by dissolving about 0.2 g of the polymer sample in 2 mL of hot DMAc. The homogeneous solution was poured into a glass Petri dish, which was placed in a 90^{o}C over for 3 h to release most of the solvent, and then the semidried film was further dried in vacuo at 160^{o}C for 6 h. The obtained films were used for solubility and thermal analyses.

Measurements

Infrared (IR) spectra were recorded using a Horiba FT-720 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance III HD-600 MHz NMR spectrometer. Inherent viscosities were determined with a Cannon-Fenske viscometer at 30°C. Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer Pyris 1 TGA, analyzing approximately 3−5 mg of polymer film samples heated in flowing nitrogen or air (flow rate = 40 cm^3/min) at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analyses were conducted on a Perkin-Elmer DSC 4000 at a scan rate of 20 °C/min in flowing nitrogen. Electrochemical measurements were performed with a CHI 750A electrochemical analyzer. Cyclic voltammetry was presented with the positive potential oriented to the left and increasing anodic currents directed downwards. The experiments utilized a three-electrode cell, where ITO (with polymer film dimensions of approximately 0.5 cm × 2.0 cm) served as the working electrode. All cell potentials were measured using a home-made Ag/AgCl, KCl (saturated) reference electrode. Ferrocene was employed as an external reference for calibration (+0.44 V vs. Ag/AgCl). Spectroelectrochemical analyses were conducted with an electrolytic cell comprising a 1 cm cuvette, ITO as the working electrode, a platinum wire as the auxiliary electrode, and a home-made Ag/AgCl, KCl (saturated) reference electrode. Absorption spectra in the spectroelectrochemical experiments were measured using an Agilent 8453 UV-visible photodiode array spectrophotometer.

Fabrication of Electrochromic Devices

Electrochromic polymer films were prepared by depositing a solution of the polymers (3.5 mg/mL in DMAc) onto ITO-coated glass with an area of 2 cm × 2.5 cm. A gel electrolyte was formulated using poly(methyl methacrylate) (PMMA) (Mw: 120,000) and $LiClO_4$, plasticized with propylene carbonate (PC) to create a highly transparent and conductive gel. To prepare the gel, 1 g of PMMA was dissolved in 4 mL of dry acetonitrile, and 0.1 g of $LiClO_4$ was added as a supporting electrolyte. Next, 1.5 g of propylene carbonate was incorporated as a plasticizer. The mixture was gently heated until gelation occurred. The resulting gel electrolyte was then applied to the polymer-coated side of the electrode, after which the electrodes were sandwiched together.

References

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[S2] S.-H. Hsiao and L.-R. Dai, Synthesis and properties of poly(ether imide)s based on the bis(ether anhydride)s from hydroquinone and its derivatives, *J. Polym. Sci. Part A: Polym. Chem.*, 1999, **37**, 665−675.
[S3] H.-J. Yen and G.-S. Liou, Solution-processable novel near-infrared electrochromic aromatic polyamides based on electroactive tetraphenyl-*p*-phenylenediamine moieties, *Chem. Mater.*, 2009, **21,** 4062–4070.
[S4] J.-H. Huang and K.-C. Lee, Highly stable, solution-processable phenothiazine derivative as hole collection material for organic solar cells, *ACS Appl. Mater. Interfaces*, 2014, **6**, 7680–7685.
[S5] X. Liao, H. Zhang, J. Huang, G. Wu, X. Yin and Y. Hong, (D−π−A) 3−Type metal-

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Table S1 Inherent viscosity and solubility behavior of polyamides

Polymer code	η_{inh} (dL/g)[a]	Solvents[b,c]					
		DMF	DMAc	DMSO	NMP	THF	*m*-Cresol
6a	0.14	++	++	++	++	++	++
6b	0.17	++	++	++	++	+	++
6c	0.31	++	++	++	++	++	+

Table S2 Inherent viscosity and solubility behavior of polyimides

Polymer code	η_{inh} (dL/g)[a]		Solvents[b,c]					
	PAA	PI	DMF	DMAc	DMSO	NMP	THF	*m*-Cresol
8a	0.30	0.20	++	++	+–	++	++	+–
8b	0.43	0.27	+–	+	–	++	+	+
8c	0.39	0.29	+	+	–	++	+	+

[a] Inherent viscosity measured at a concentration of 0.5 dL/g in DMAc at 30 °C. PAA: poly(amic acid).

[b] The qualitative solubility was tested with 10 mg of a sample in 1 mL of stirred solvent. ++: soluble at room temperature; +: soluble on heating; +– : partially soluble; – : insoluble even on heating.

[c] Solvent: DMF: *N,N*-dimethylformamide; DMAc: *N,N*-dimethylacetamide; DMSO: dimethyl sulfoxide; NMP: *N*-methyl-2-pyrrolidone; THF: tetrahydrofuran.

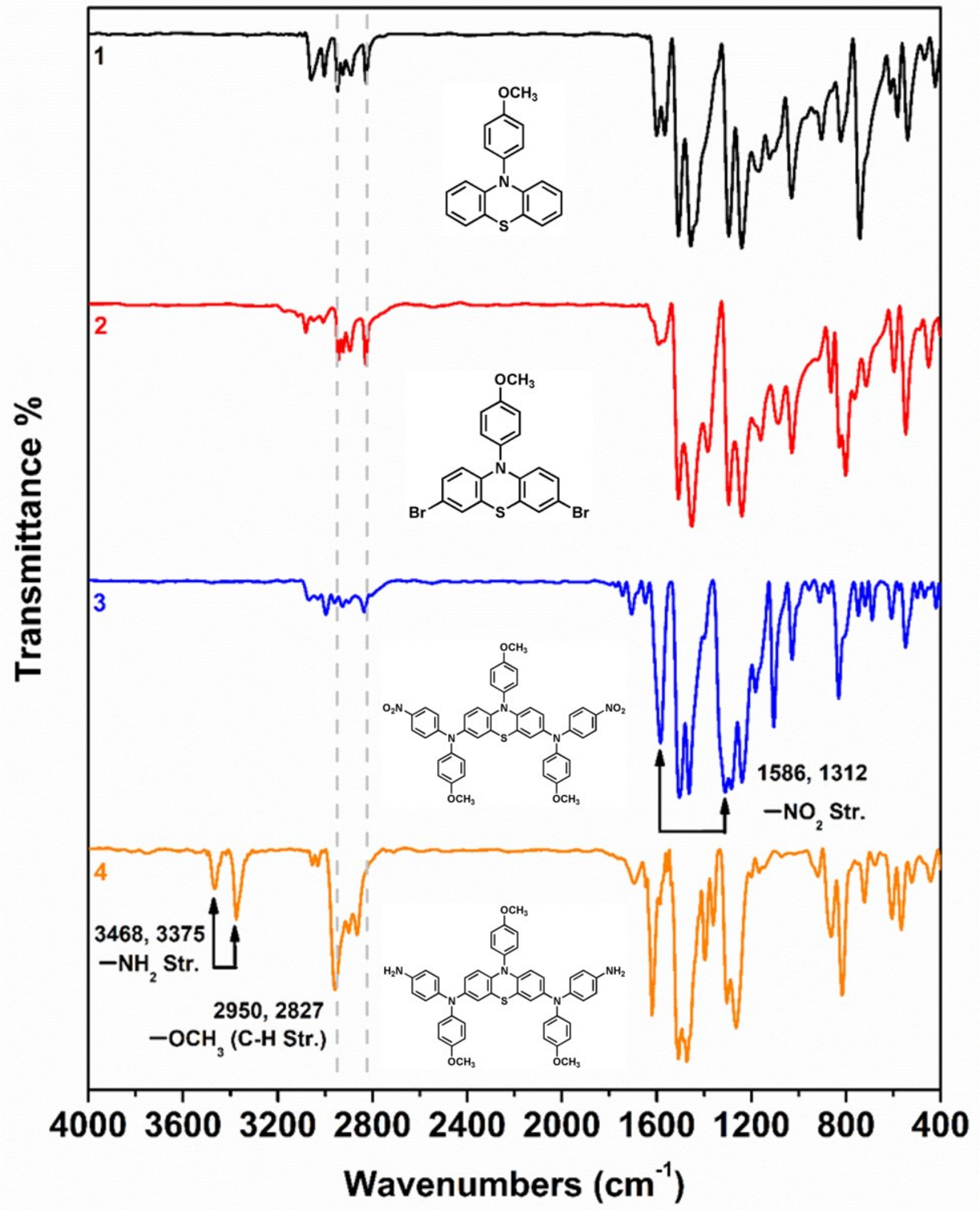

Fig. S1 IR spectra of diamine monomer **4** and its precursor compounds.

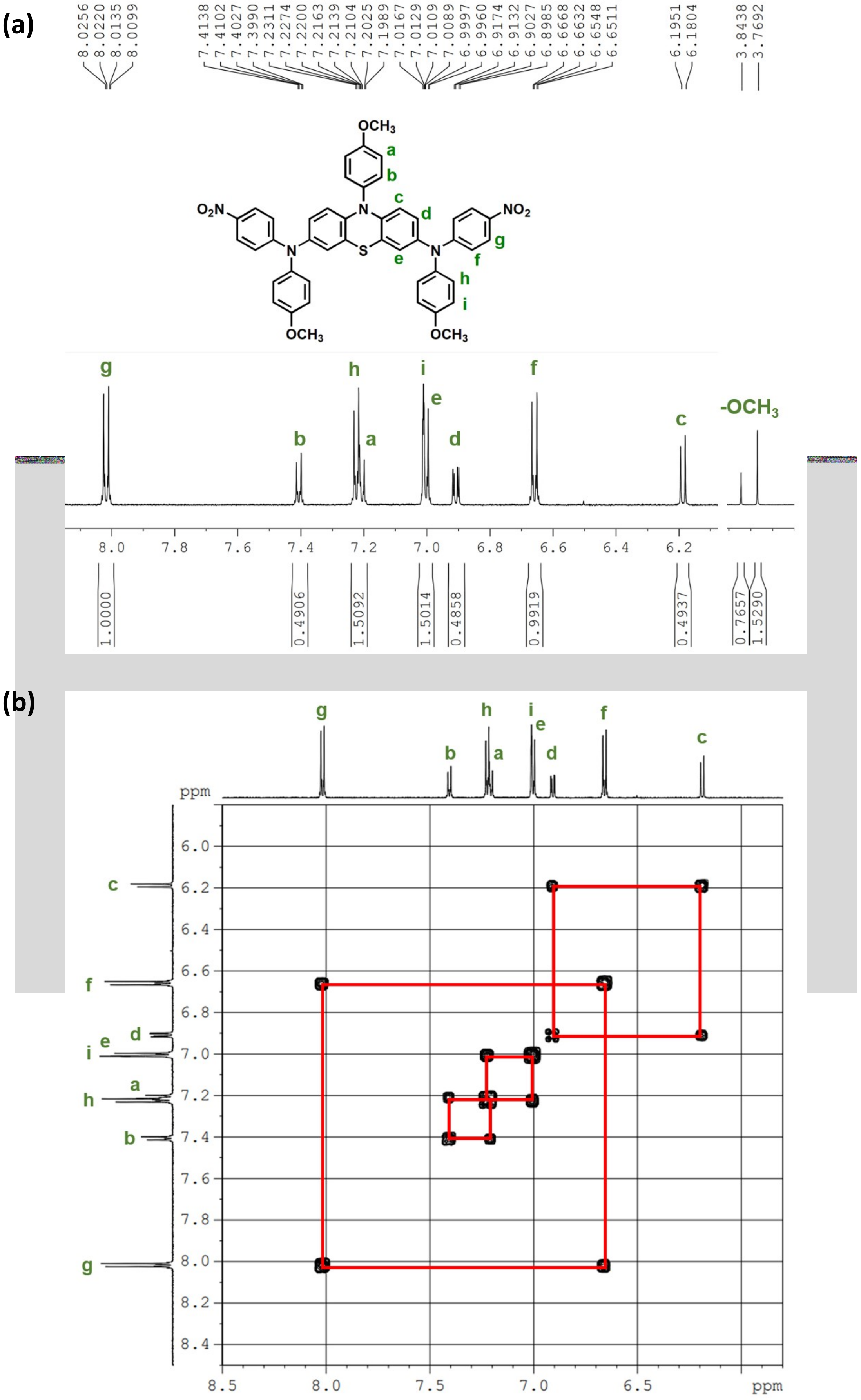

Fig. S2 (a) ^{1}H NMR and (b) H-H COSY spectra of dinitro compound **3** in DMSO-d_6.

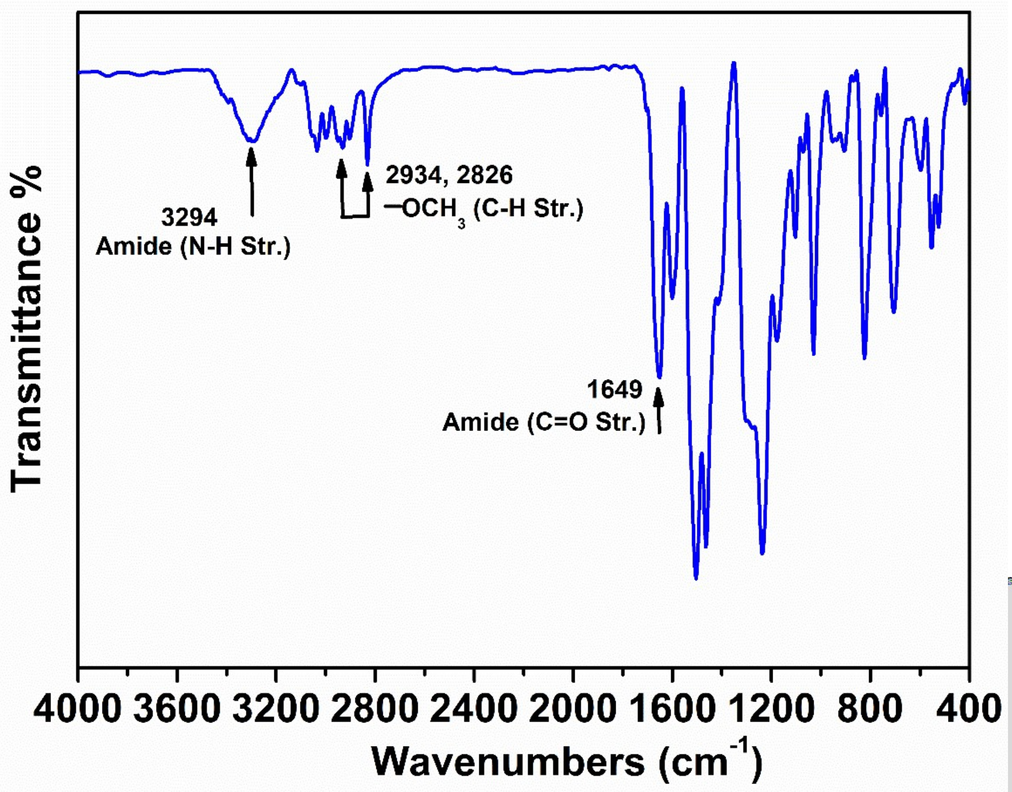

Fig. S3 The IR spectrum of model compound **M1.**

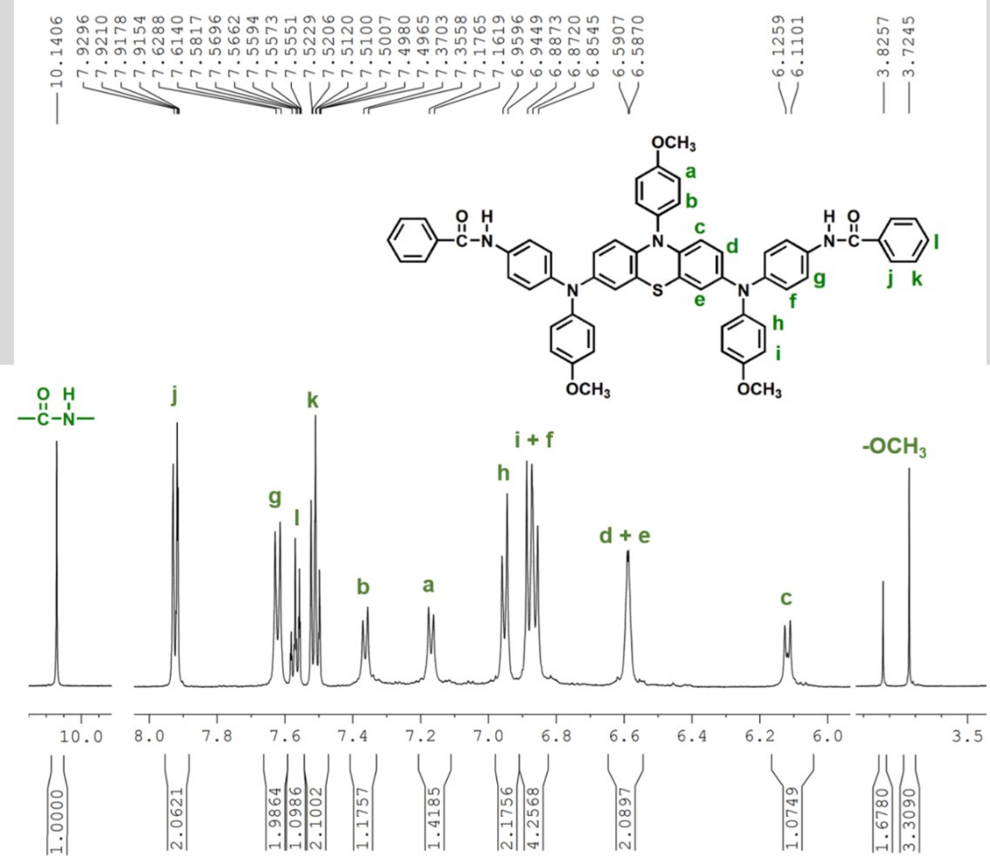

Fig. S4 The proton NMR spectrum of model compound **M1** in DMSO-d_6.

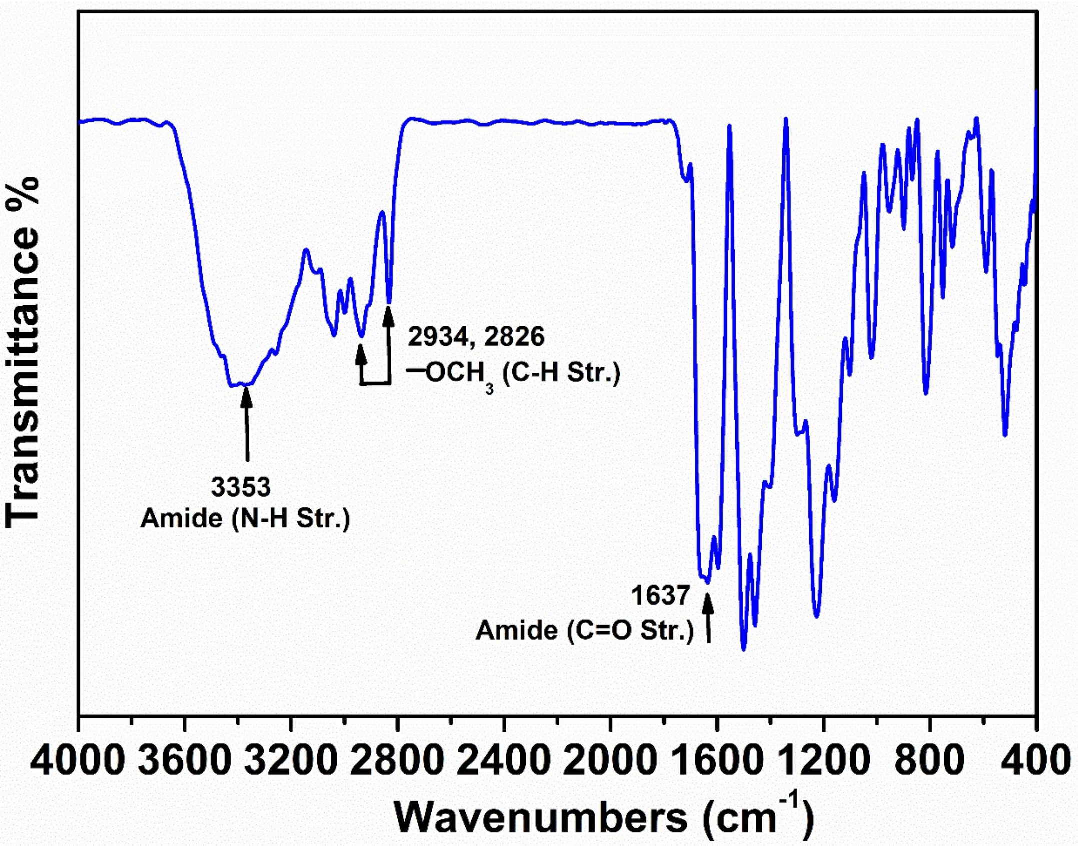

Fig. S5 The IR spectra of polyamide **6b**.

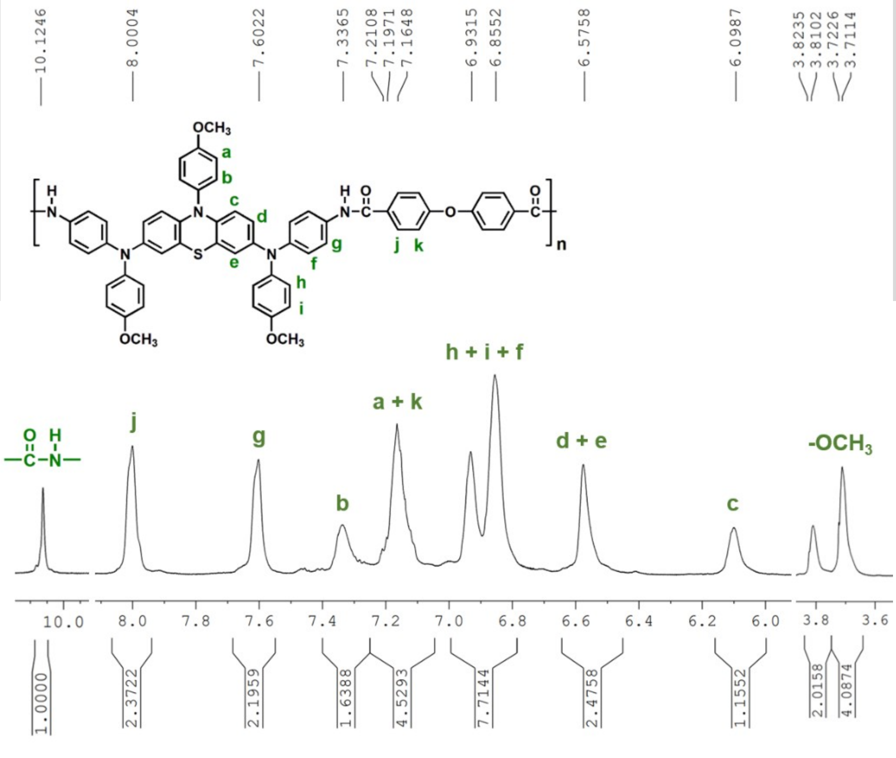

Fig. S6 The ^{1}H NMR spectrum of polyamide **6b** in DMSO-d_6.

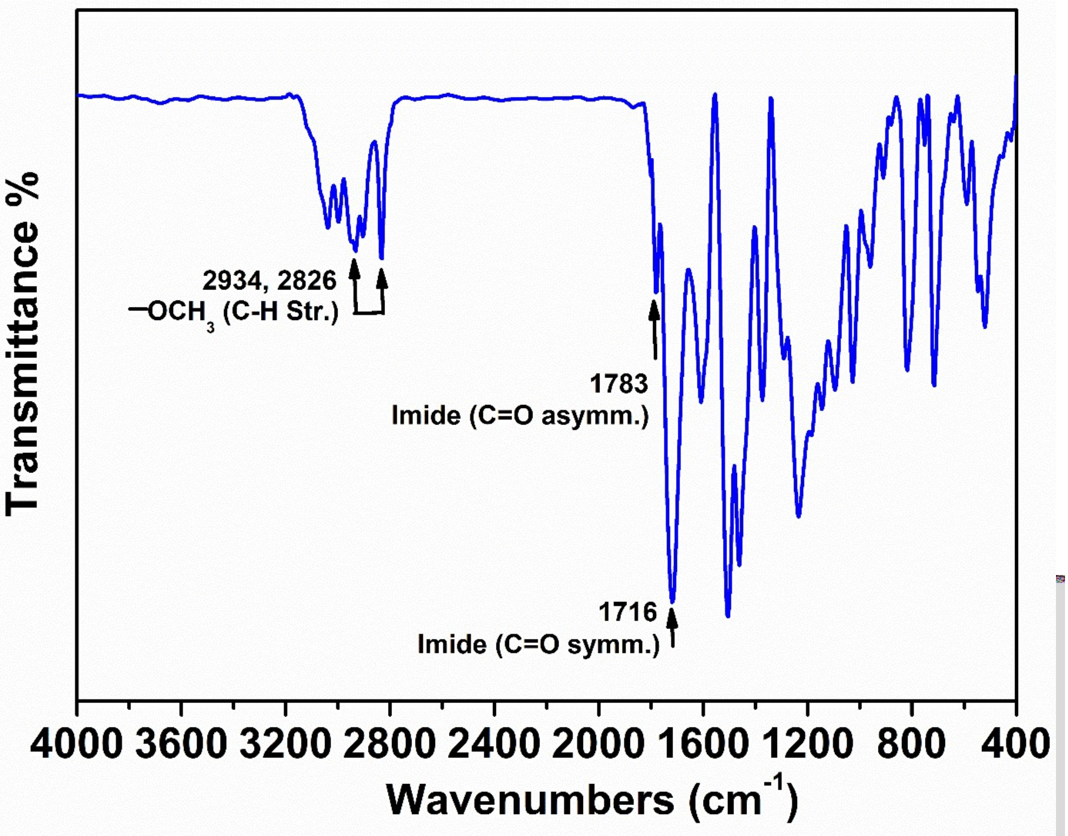

Fig. S7 The IR spectra of polyimide **8a**.

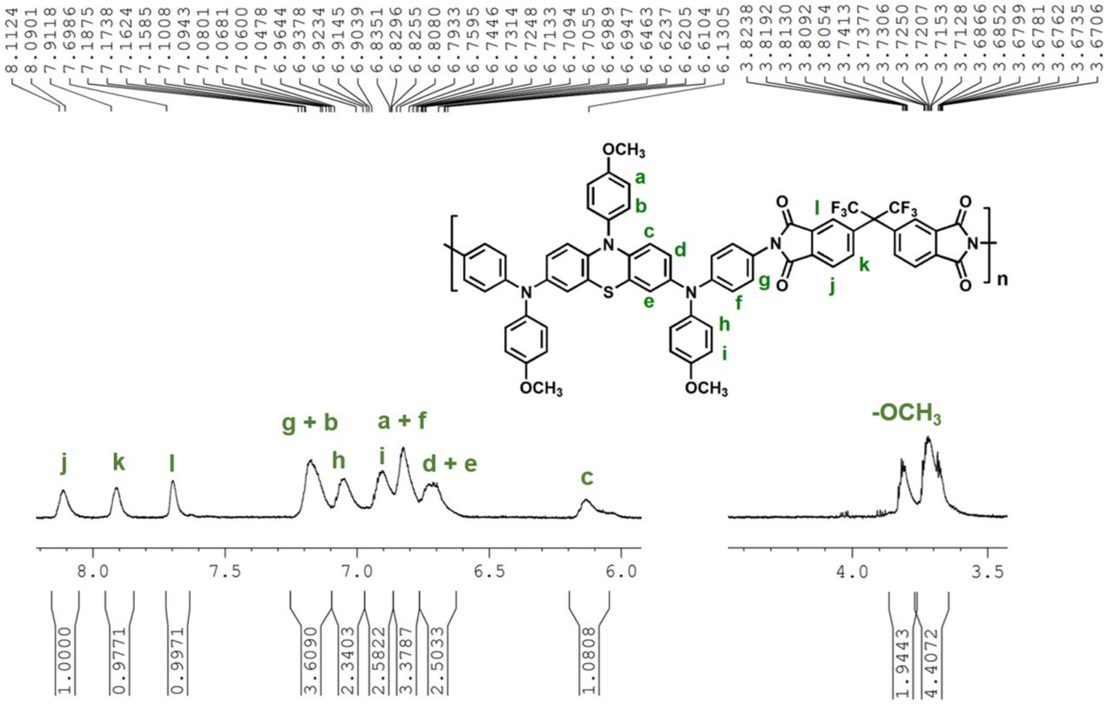

Fig. S8 The ^{1}H NMR spectrum of polyimide **8a** in DMSO-d_6.

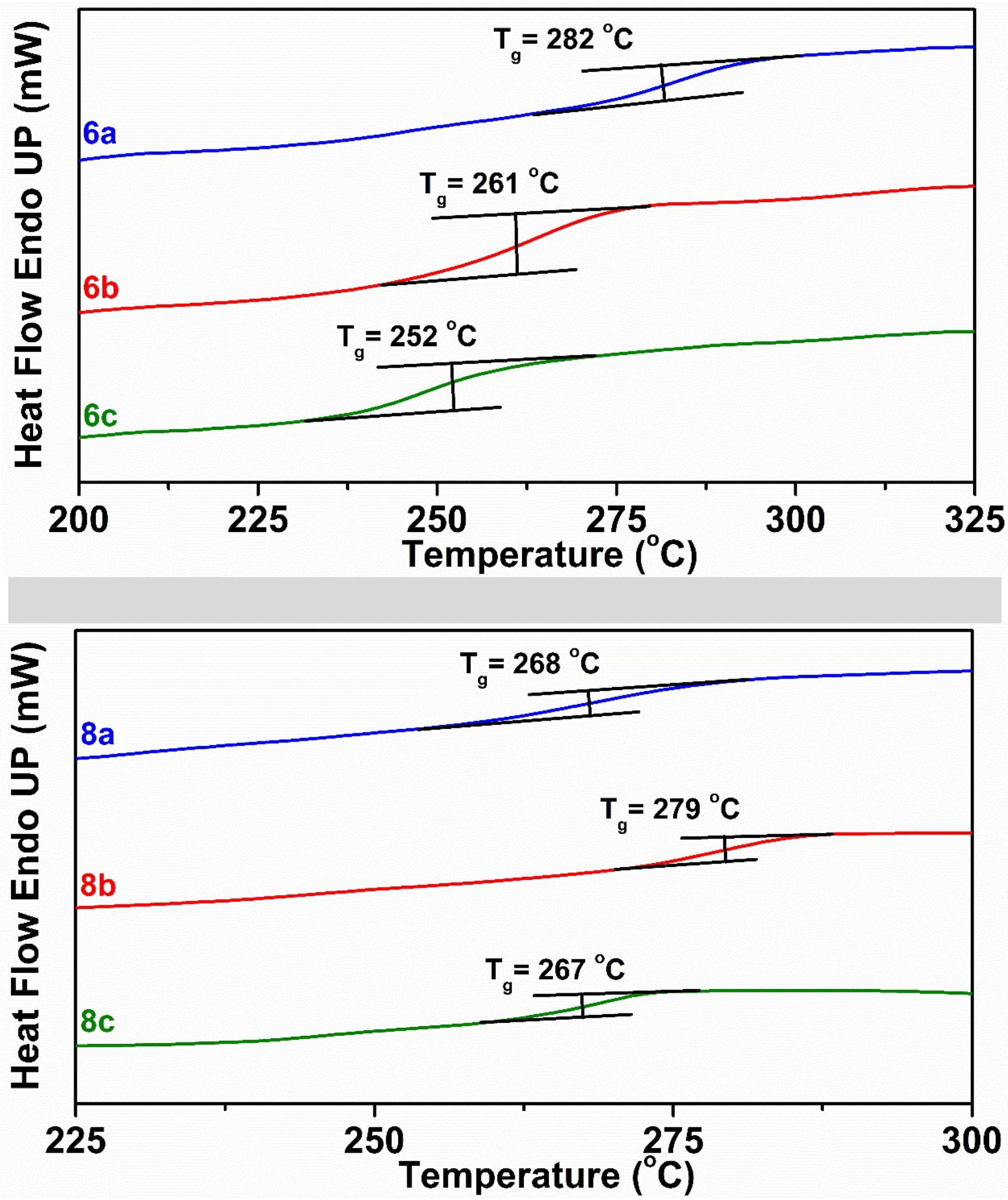

Figure S9 DSC thermograms of the polymers with a heating rate of 20°C min^{-1} in nitrogen.

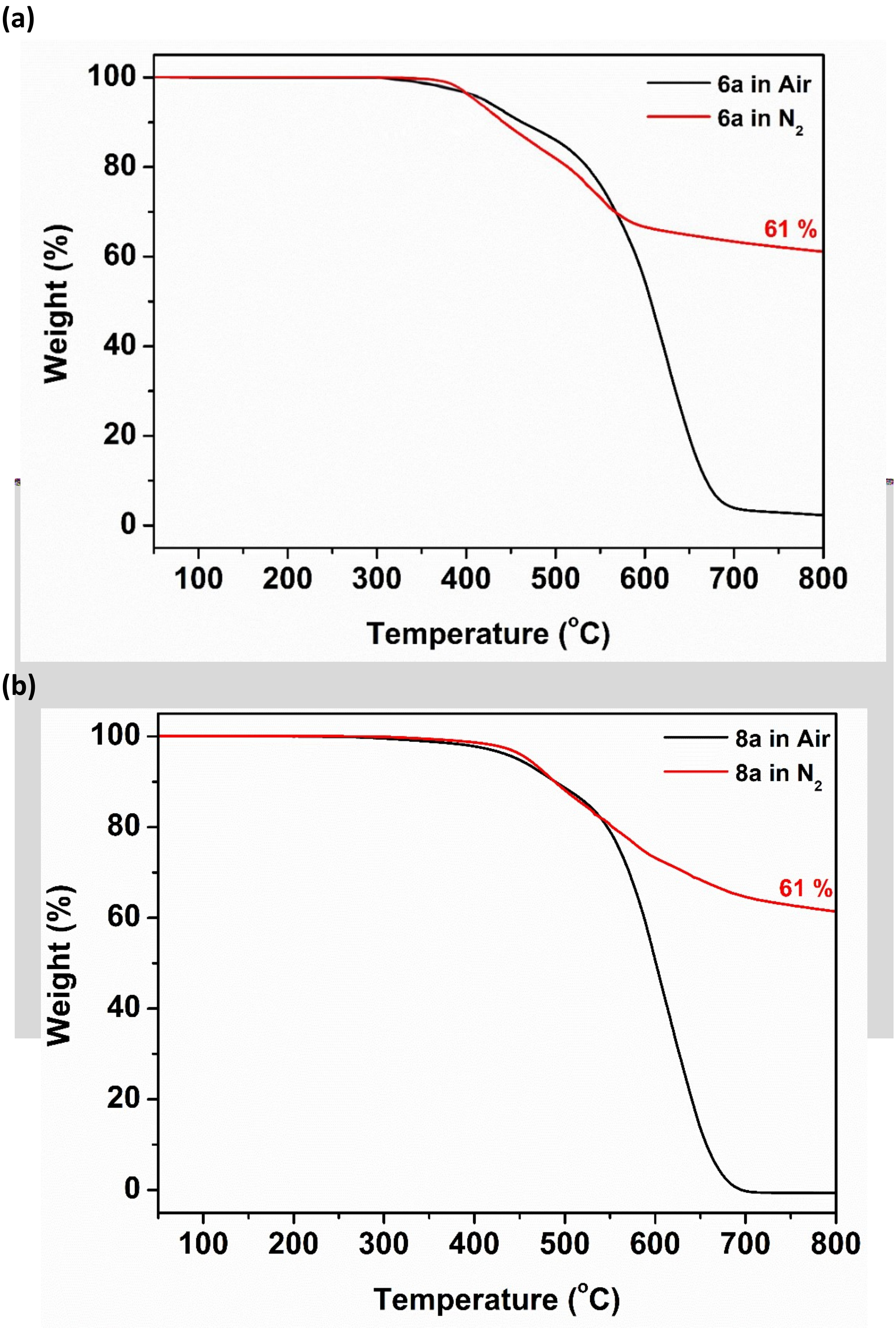

Figure S10 TGA thermograms of (a) polyamide **6a** and (b) polyimide **8a** with a heating rate of 20°C min^{-1}.

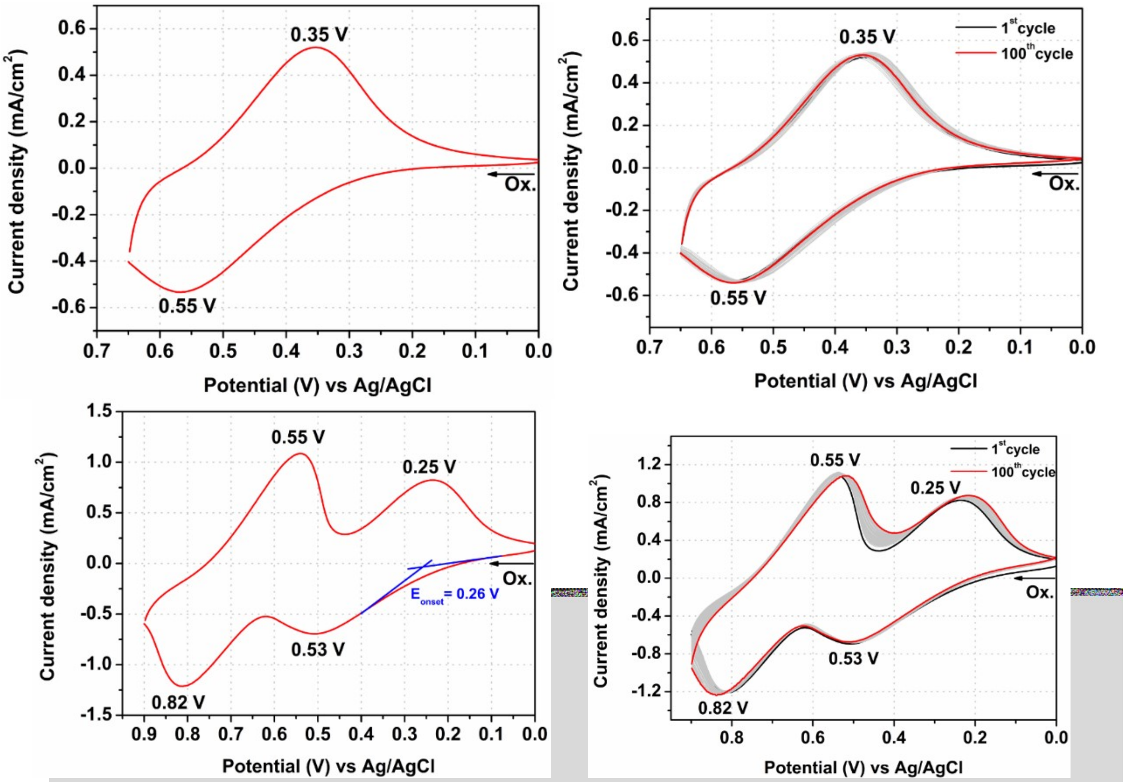

Figure S11 CV diagrams of the cast film of polyamide **6a** on ITO-glass substrate immersed in 0.1 M Bu_4NClO_4/MeCN at a scan rate of 50 mV s^{-1}. Left: the first scans; right: comparison between the first and the 100th scans.

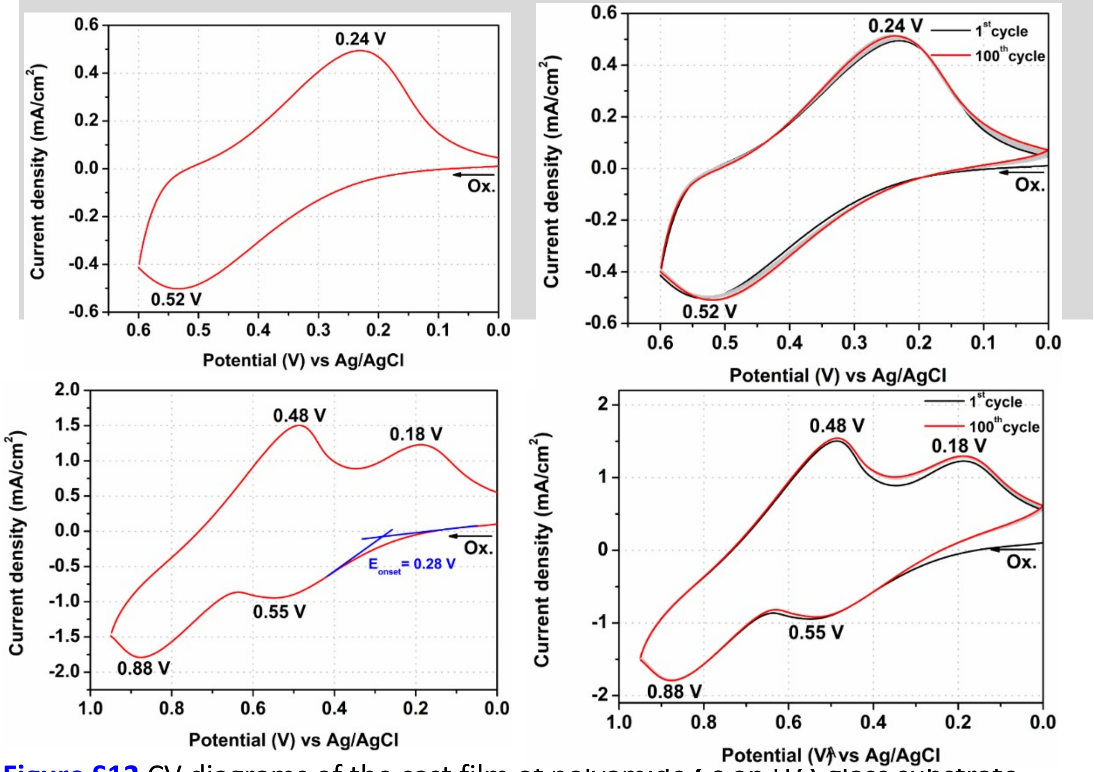

Figure S12 CV diagrams of the cast film of polyamide **6c** on ITO-glass substrate immersed in 0.1 M Bu_4NClO_4/MeCN at a scan rate of 50 mV s^{-1}. Left: the first scans; right: comparison between the first and the 100th scans.

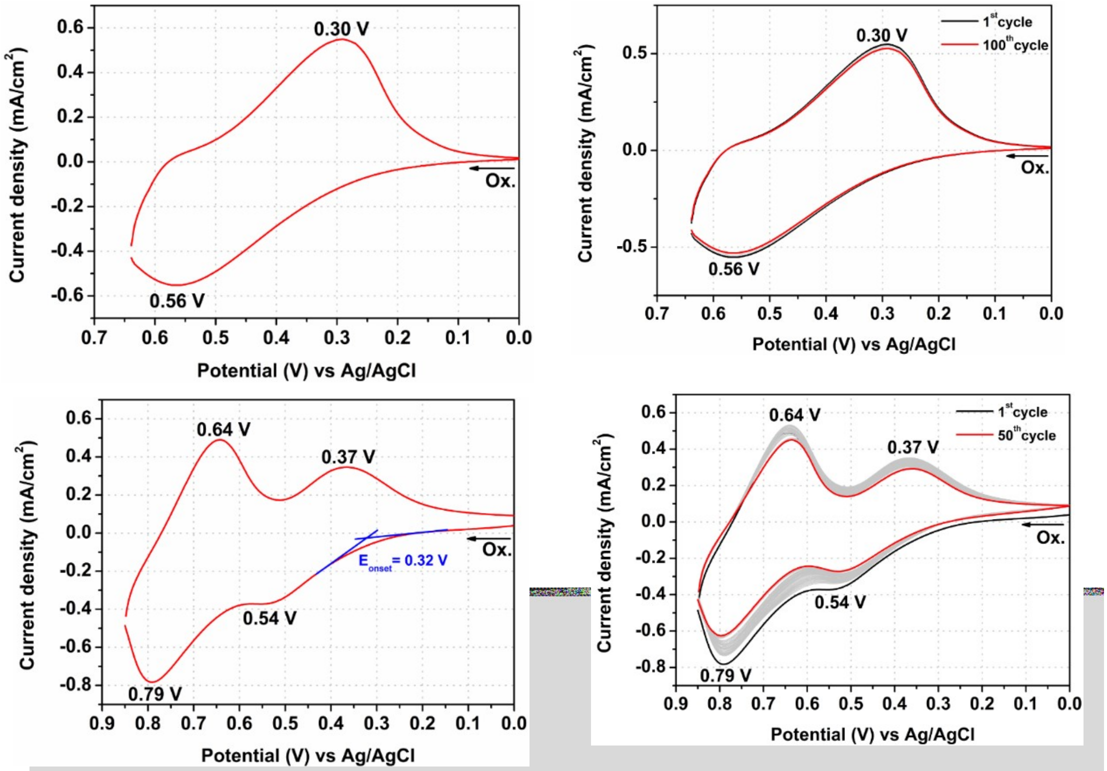

Figure S13 CV diagrams of the cast film of polyimide **8a** on ITO-glass substrate immersed in 0.1 M Bu_4NClO_4/MeCN at a scan rate of 50 mV s^{-1}. Left: the first scans; right: comparison between the first and the 100th scans.

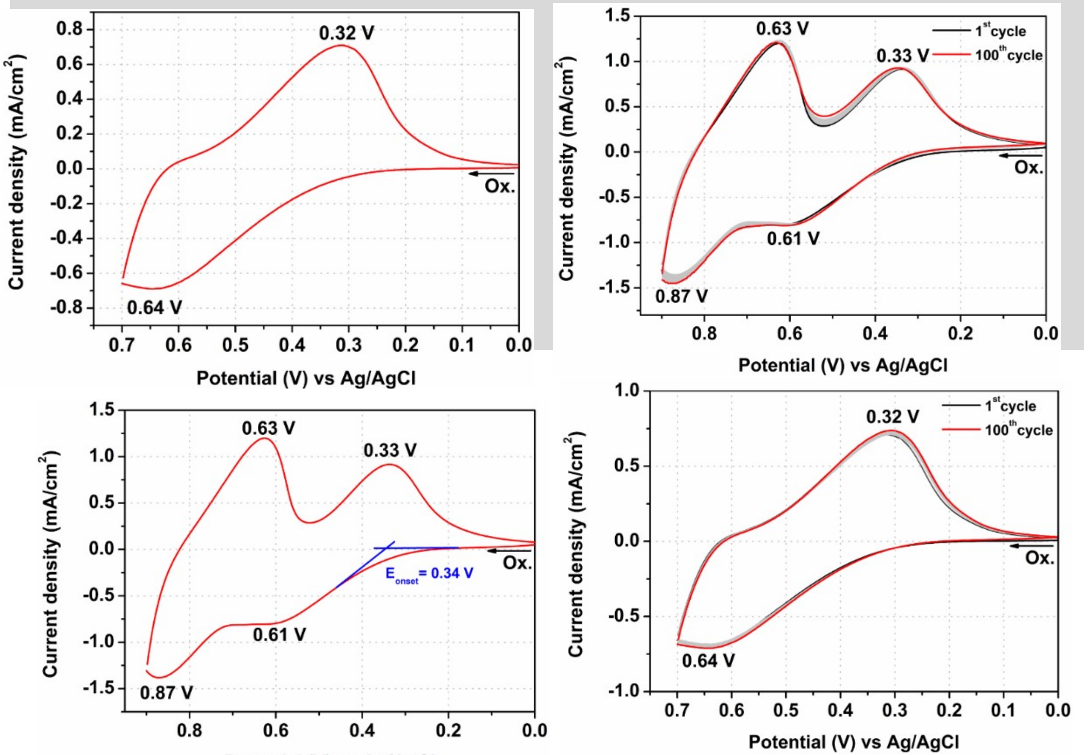

Figure S14 CV diagrams of the cast film of polyimide **8c** on ITO-glass substrate immersed in 0.1 M Bu_4NClO_4/MeCN at a scan rate of 50 mV s^{-1}. Left: the first scans; right: comparison between the first and the 100th scans.

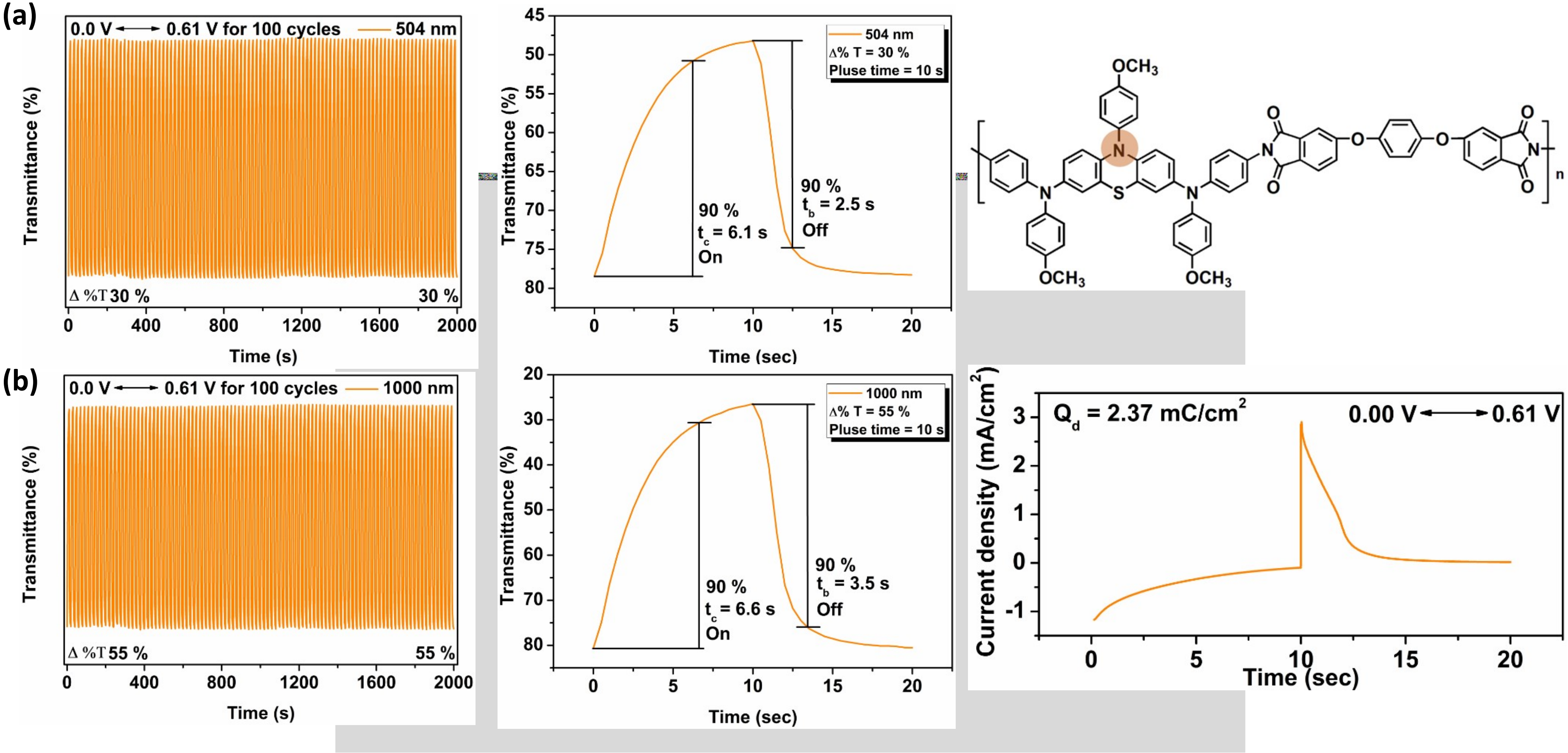

Figure S15 Left: Electrochromic switching responses of the cast film of polyimide **8c** on the ITO-glass slide (coated area ~ 0.8 x 2.2 cm^2) in 0.1 M Bu_4NClO_4/MeCN by applying a potential step: potential 0.00 V ⇆ 0.61 V with pulse width of 10 s, monitored at (a) λ_{max} = 504 nm and (b) λ_{max} = 1000 nm. Middle: calculation of optical switching time from the first cycle. Right: Ejected charge (Q_d) calculated from the first cycle.

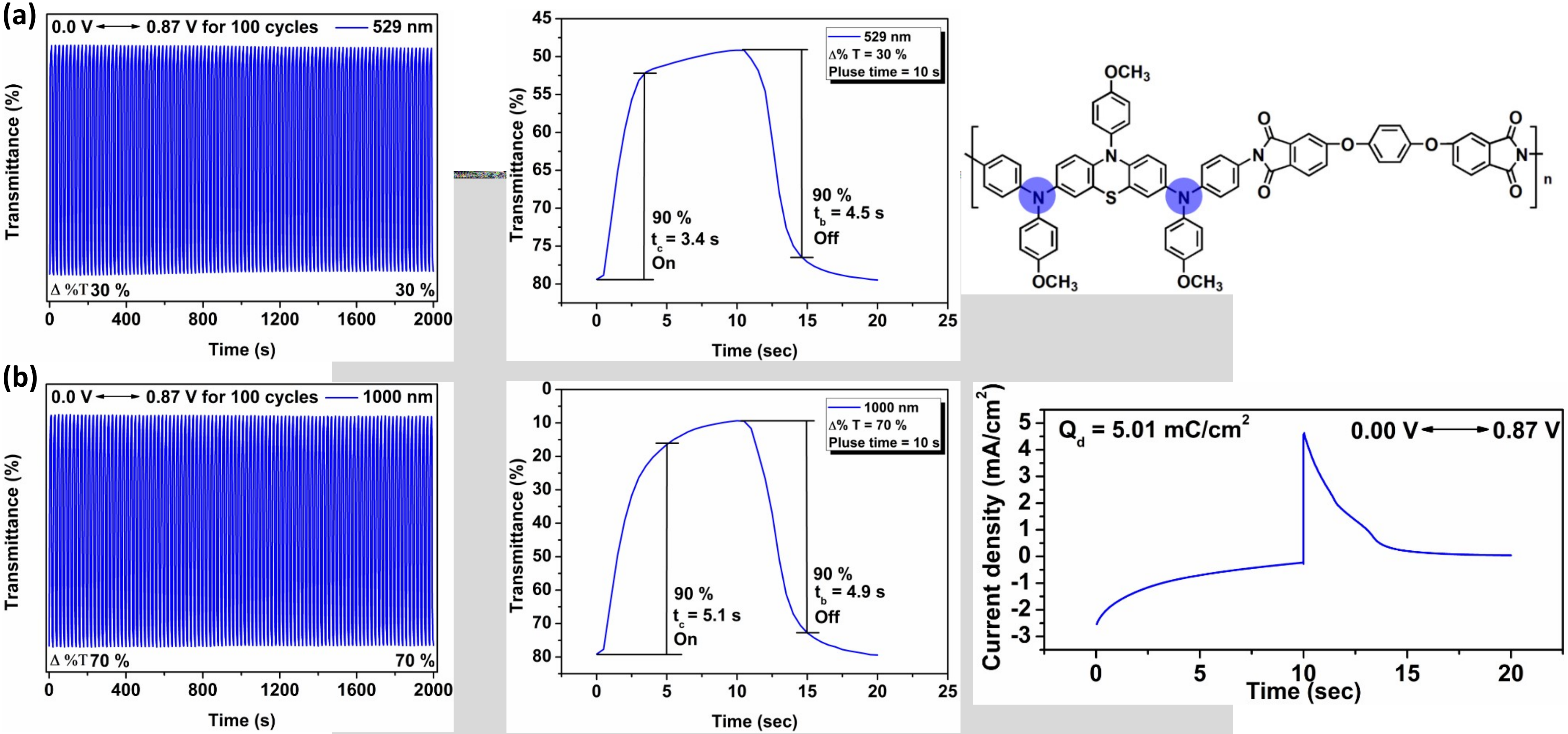

Figure S16 Left: Electrochromic switching responses of the cast film of polyimide **8c** on the ITO-glass slide (coated area ~ 0.8 x 2.2 cm^2) in 0.1 M Bu$_4$NClO$_4$/MeCN by applying a potential step: potential 0.00 V ⇆ 0.61 V with pulse width of 10 s, monitored at (a) λ_{max} = 529 nm and (b) λ_{max} = 1000 nm. Middle: calculation of optical switching time from the first cycle. Right: Ejected charge (Q$_d$) calculated from the first cycle.