Supporting Information

Novel Triarylamine-based Polybenzoxazines with Donor-Acceptor System for Polymeric Memory Devices

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Experimental Section

Materials

4,4'-Diamino-4''-methoxytriphenylamine[1a] (**1**, mp = 148-149 °C) and *N,N'*-bis(4-aminophenyl)-*N,N'*-di(4-methoxylphenyl)-1,4-phenylenediamine[1b] (**2**, mp = 206-209 °C) were synthesized according to the previously reported procedures.

Synthesis of Polybenzoxazine Precursors

The synthesis of **TPA-BPS** was used as an example to illustrate the general synthetic route for the resulting PB precursor. 1.0 g (3.27 mmole) of **1**, 0.82 g (3.27 mmole) 4,4′-sulfonyldiphenol (BPS), and 9.0 mL a mixed solvent of toluene/ethanol (2/1, v/v) were introduced into a round-bottom 50 ml glass flask equipped with a nitrogen inlet, a condenser, and a magnetic stirrer. 0.39 g (13.08 mmole) of paraformaldehyde was added to the reaction mixture after heating the temperature to 70 °C. The mixture was stirred at 90 °C for 9 hours. The solution was then poured into methanol. The precipitate was filtered and washed in methanol at room temperature. After drying at 80 °C in vacuum oven, brown powder (1.73 g, 91% yield) was obtained. ^{1}H NMR (DMSO-d_6, δ, ppm): 3.66 (s, 3H, OCH_3), 4.64 (s, 4H, N-CH_2-Ar), 5.42 (s, 4H, N-CH_2-O), 6.75 (d, 4H), 6.82 (m, 3H), 6.89 (m, 4H), 6.96 (d, 2H), 7.58 (d, 2H), 7.70 (d, 3H).

Preparation of Polybenzoxazine Thick Films

The preparation of **P(TPA-BPS)** was used as an example to illustrate the general route used to produce the thermoset PBs thick films. A 25wt% PB precursor in *N*-methyl-2-pyrrolidone (NMP) solution was prepared. The solution was then cast onto glass by automatic film applicator, and dried at 100 °C for 3 h, then cured at 120 °C for 2h, 140 °C for 1 h, 160 °C for 1 h, 180 °C for 1 h, 200 °C for 1 h, 220 °C for 1 h, and 240 °C for 1h in vacuum. The obtained thin film was about 40±5 μm thick and was used for tests of thermal properties

Preparation of Polybenzoxazine Precursor Thin Films

The preparation of **TPA-BPS** was used as an example to illustrate the general route used to produce the thermoset thin films of PB precursors. A solution was prepared by dissolving the PB precursor, **TPA-BPS**, in *N,N*-dimethylacetamide (DMAc) at a concentration around 60 mg mL^{-1}. The solution was filtered through a 0.2 μm syringe filter before it was spin-coated at 1000 rpm for 60 seconds onto indium tin oxide (ITO) glass substrate and dry at room temperature. The obtained thin films with thickness of 120± 10 nm were used for

electrochemical and optical tests. On the other hand, a solution of 38 mg mL^{-1} was used for the preparation of thin films with 50± 3 nm in thickness for memory measurement.

Preparation of Polybenzoxazine Thin Films

The preparation of **P(TPA-BPS)** was used as an example to illustrate the general route used to produce the thermoset PBs thin films. PB thin films, **P(TPA-BPS)**, were prepared by curing the thin film of PB precursor, **TPA-BPS**, at the heating program of 100 °C for 1h, 120 °C for 1h, 140 °C for 1h, 160 °C for 1h, 180 °C for 1h, 200 °C for 1h, 220 °C for 1h, and 240 °C for 1h in vacuum. The obtained thin films with thickness of 120± 10 nm were used for electrochemical and optical tests. In addition, the obtained thin films with thickness of 50± 3 nm were used for tests of memory behaviors.

Fabrication of Memory Devices

The memory device was fabricated with the configuration of ITO/thin film/Al as shown in Fig. 1. The ITO glasses used for memory device were precleaned by ultrasonication with water, acetone, and isopropanol each for 15 min. After cleaning the ITO glasses, thin films of the resulting polymers were prepared on the ITO glasses the by above-mentioned procedure. Finally, a 300-nm-thick Al top electrode was thermally evaporated through the shadow mask (recorded device units of 0.5 × 0.5 mm^2 in size) at a pressure of 10^{-7} torr with a uniform depositing rate of 3-5 Å/s.

Theoretical Calculation

The theoretical calculation in this study was performed by Gaussian 09 program package. The results of value and distributions of the corresponding energy levels within each basic unit of the TPA-based and TPPA-based PBs and PB precursors were investigated via density functional theory (DFT) method at the B3LYP level of theory (Beckesstyle three-parameter density functional theory using the Lee-Yang-Parr correlation functional) with the 6-31G(d) basic set.

Measurements

^{1}H NMR spectra were measured on a Bruker AVANCE-600 FT-NMR using tetramethylsilane as the internal standard, and peak multiplicity was reported as follows: s, singlet; d, doublet. The inherent viscosities were determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 °C. Gel permeation chromatographic (GPC) analysis was carried out on a

Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Waters 5 μm Styragel HR-2 and HR-4 columns (7.8 mm I. D. × 300 mm) were connected in series with NMP as the eluent at a flow rate of 0.5 ml/min at 40 ^{o}C and were calibrated with polystyrene standards. For temperature scanning, DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 10 ^{o}C/min in flowing nitrogen (20 cm^3/min). Thermogravimetric analyses (TGA) were conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 3-5 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm^3/min) at a heating rate of 20 ^{o}C/min. Thermal Mechanical Analyzer (TMA) was conducted with a TA instrument TMA Q400. The TMA experiments were measured at a scan rate of 10 ^{o}C /min with a film/fiber probe under an applied constant load of 50 mN. Dynamic mechanical thermal analysis (DMTA) was performed using a DMA 2980, TA Instruments (USA), at a heating rate of 3 ^{o}C min^{-1} with a load frequency of 1 Hz in a tension mode in air. Electrochemistry was performed with a CH Instruments 612C electrochemical analyzer. Voltammograms were presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry (CV) was conducted with the use of a three-electrode cell in which glassy carbon as working electrode in dichloromethane (CH_2Cl_2) (solution-typed CV) or the cast film on an ITO (the area of the resulting polymers thin films were about 2.0 cm x 0.8 cm) coated glass slide as working electrode in anhydrous acetonitrile (CH_3CN) (film-typed CV). A platinum wire was used as an auxiliary electrode. All cell potentials were taken by using a homemade Ag/AgCl, KCl (sat.) reference electrode. UV-visible absorption was recorded on UV-visible spectrophotometer (Hitachi U-4100). The thickness of the resulting polymers thin films was measured by alpha-step profilometer (Kosaka Lab., Surfcorder ET3000, Japan). The electrical characterization of the memory device was performed by a Keithley 4200-SCS semiconductor parameter analyzer equipped with a Keithely 4205-PG2 arbitrary waveform pulse generator. ITO was used as the cathode (maintained as common), and Al was set as the anode during the voltage sweep. All *I-V* curevs were conducted in the steps of 0.1 V with 0.01 A compliance current. The probe tip used 10 μm diameter tungsten wire attached to a tinned copper shaft with a point radius <0.1 μm (GGB Industries, Inc.).

Results and Discussion

Synthesis of Polybenzoxazine Precursors

Novel PB precursors containing BPS units were synthesized by the Mannich-type polycondensation of paraformaldehyde, commercially available bisphenol (BPS), and synthesized diamines (**1** or **2**) using toluene/ethanol as co-solvent (Scheme S1). All Mannich-type polycondensation proceeded homogeneously and gave high molecular weights (Table S1). The structures of the PB precursors were confirmed by ^{1}H NMR spectra (Fig. S1). The characteristic oxazine peaks at 5.2 ppm and 4.5 ppm in ^{1}H spectra confirmed the structure of benzoxazines. However, small signals of phenolic OH at around 10.6 ppm and N-CH_2-Ar signals at 4.2 ppm were observed in the ^{1}H NMR spectra of **TPA-BPS** and **TPPA-BPS**, suggesting a slight ring opening of benzoxazine during the preparation (~8% by calculating the integration ratio). Prof. Gu investigated the influence of electronic effects from bridging groups on thermally activated polymerization of bisphenol-based benzoxazines,[2] and found that bisphenol-based benzoxazines with electron-withdrawing bridging groups resulted in the cleavage of C-O bond and the formation of a carbocation and an oxygen anion (as shown in Scheme S2). Then the active carbon atoms marked C_1 suffer electrophilic attack from the carbocation and the protons transfer to the oxygen anions to form hydroxyl groups. According to this opinion, ring-closed structure and ring-opened structure may co-exist randomly in a polymer chain of these two PB precursors containing BPS, and it is almost impossible to remove the partially ring-opened structure. Furthermore, the tough and cross-linked PB films were successfully prepared by thermally induced ring-opening reaction from the high-molecular weight PB precursors. The degree of crosslinking was confirmed by DSC and revealed the completely ring-opening reaction of **P(TPA-BPS)** and **P(TPPA-BPS)** (Fig. S2a).

Basic Characterization

The thermally induced ring-opening reaction was identified by the DSC, and the exothermic peak temperatures of **TPA-BPS** and **TPPA-BPS**, were recorded as 248 ^{o}C and 257 ^{o}C, respectively (Fig. S2a). The thermal properties of polybenzoxazine thick films were further recorded by TGA, TMA, DMA (Fig. S2), and the data of thermal behavior is summarized in Table S2.

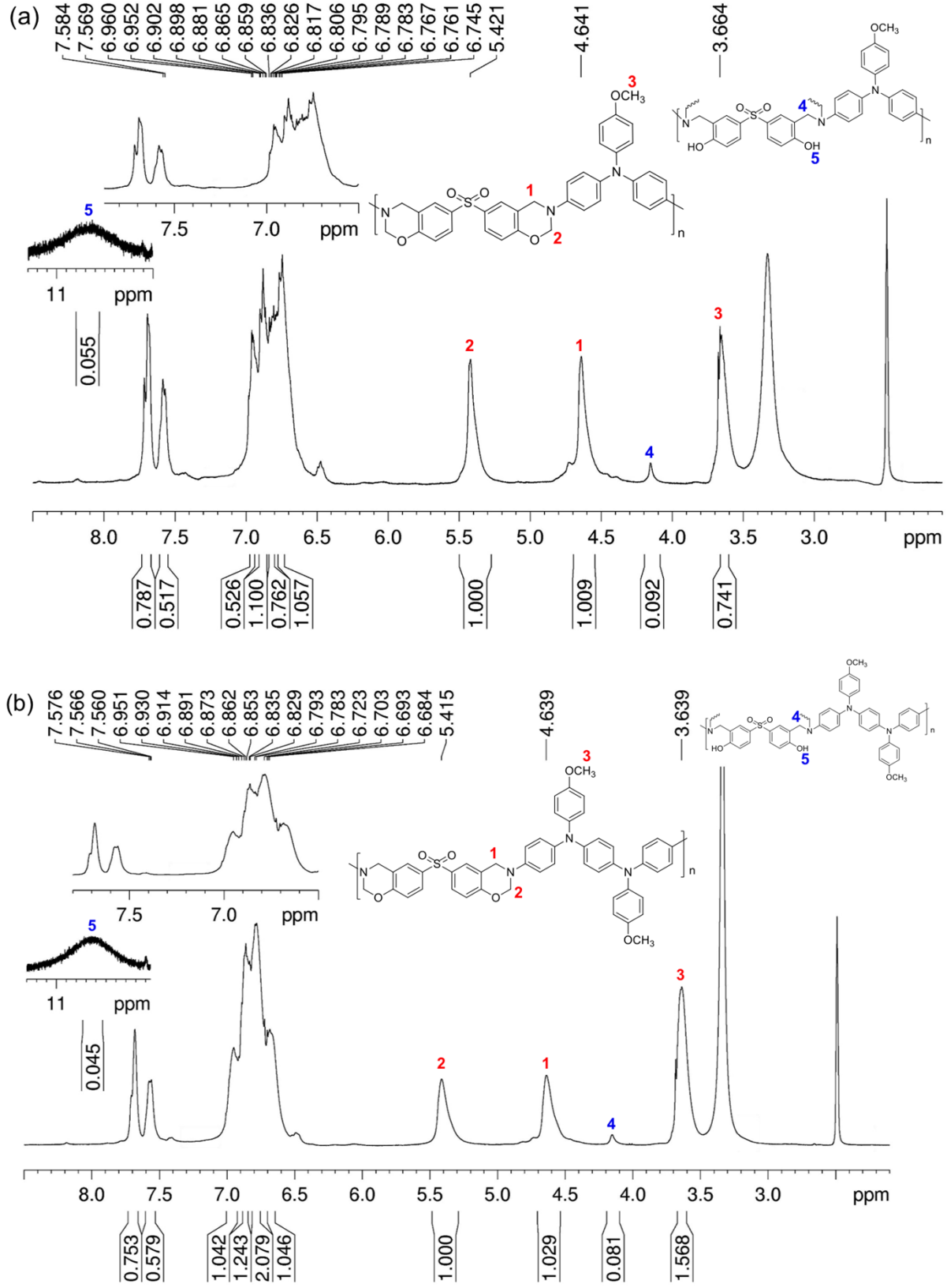


Fig. S1 ^{1}H NMR spectra of (a) **TPA-BPS** and (b) **TPPA-BPS** in DMSO-d_6.

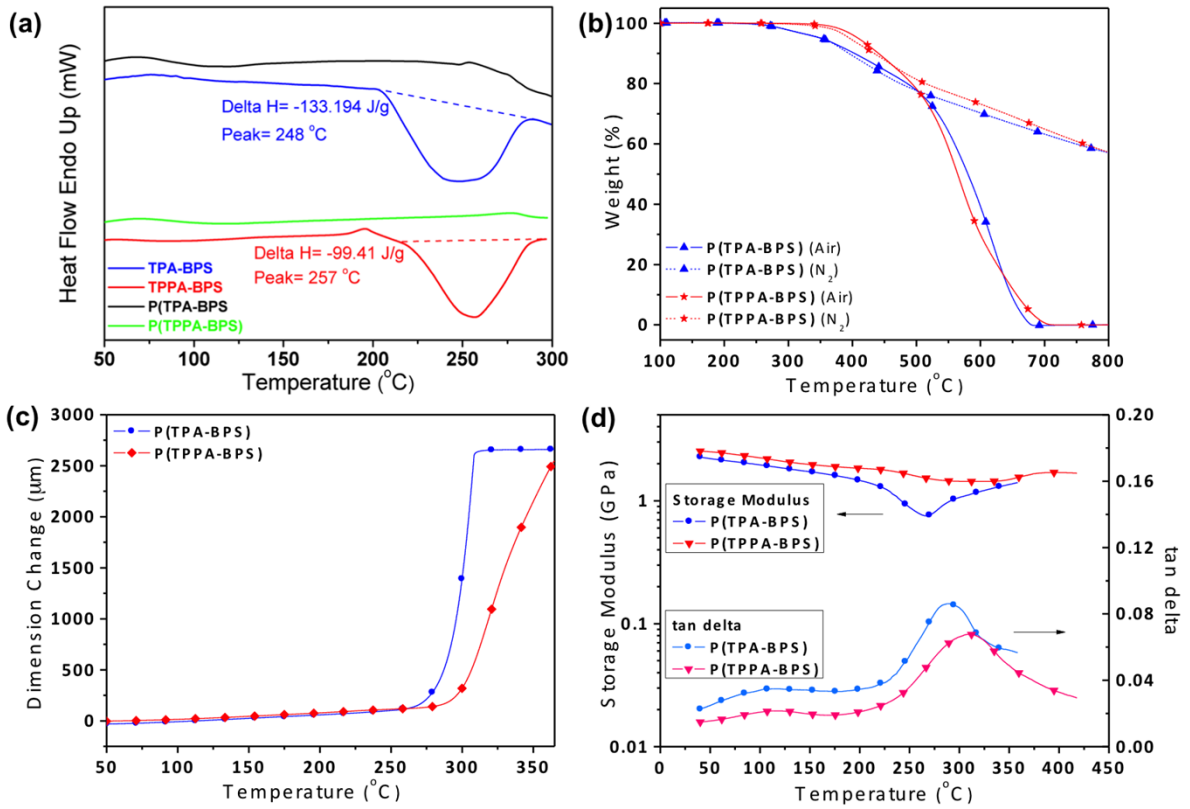


Fig. S2 (a) DSC thermograms of PB precursors and PBs, (b) TGA, (c) TMA, and (d) DMA thermograms of the cured PB films.

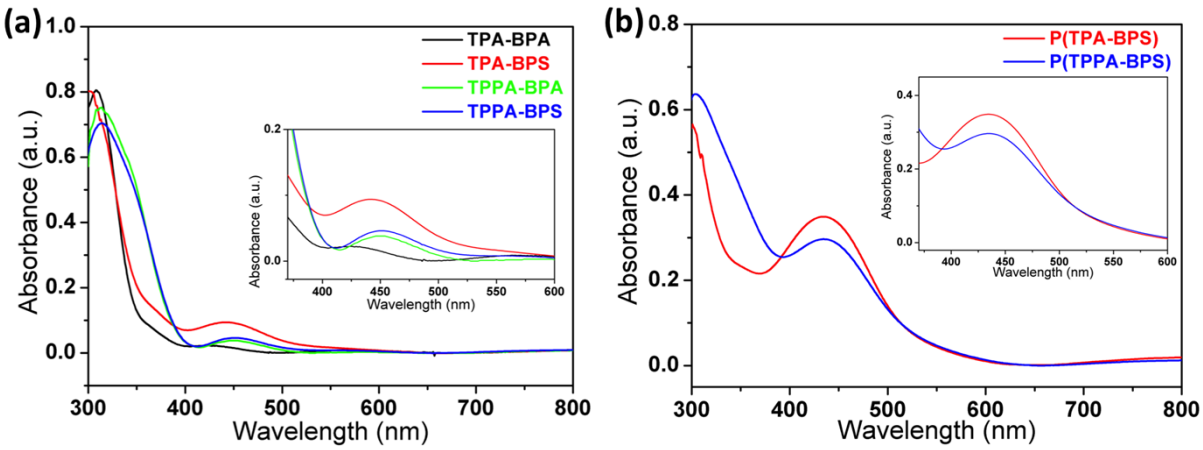


Fig. S3 UV-visible absorption spectra of (a) PB precursors and (b) BPS-based PBs.

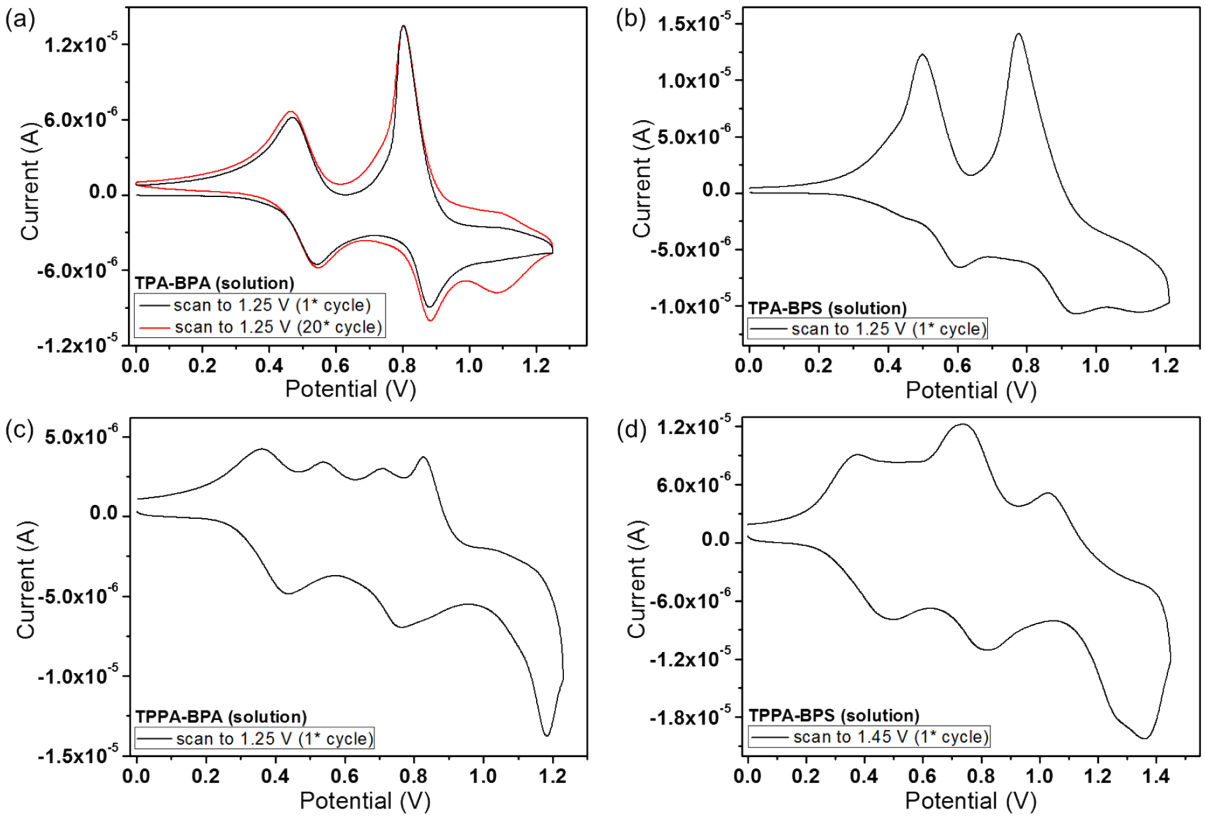


Fig. S4 CV diagram of 1 mM (a) **TPA-BPA**, (b) **TPA-BPS**, (c) **TPPA-BPA**, and (d) **TPPA-BPS** in 0.1 M TBAP/CH_2Cl_2 at a scan rate of 50 mV/s.

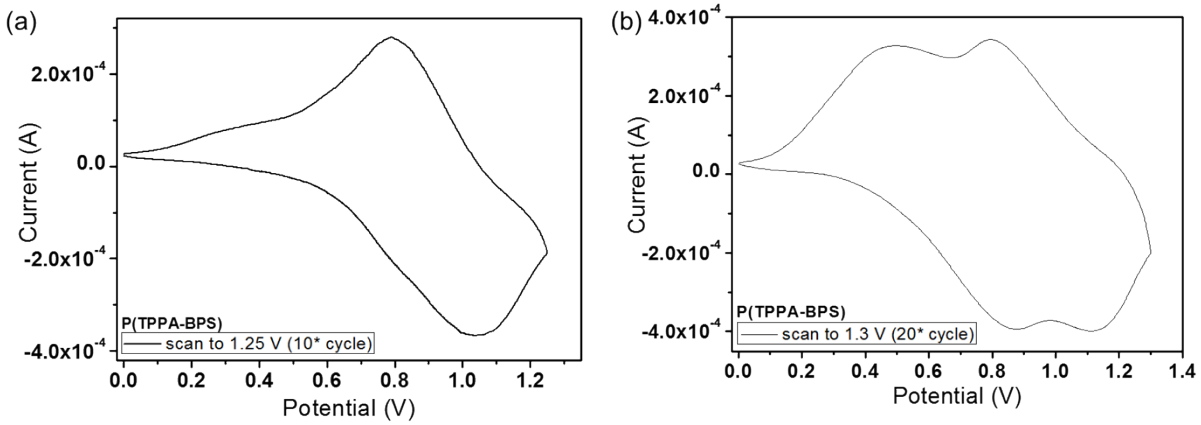


Fig. S5 CV diagrams of (a) **P(TPA-BPS)**, and (b) **P(TPPA-BPS)** film in 0.1 M TBAP/CH_3CN at a scan rate of 50 mV/s.

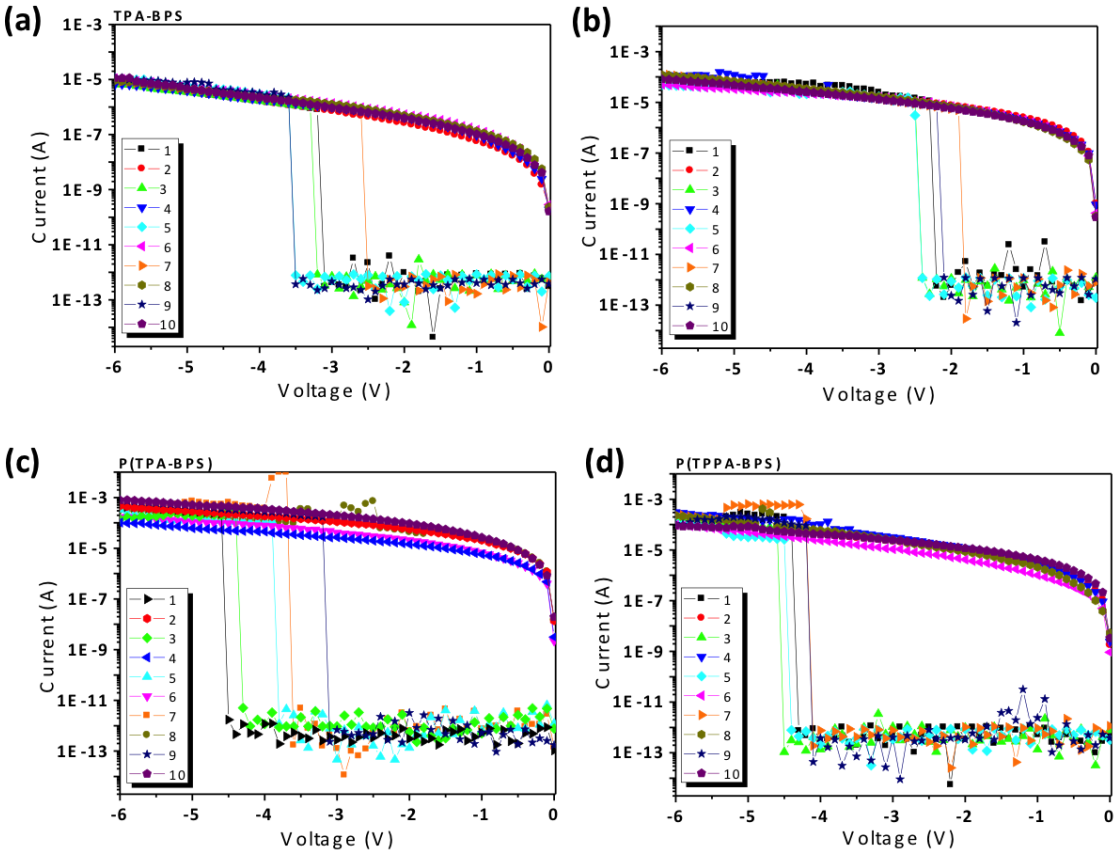
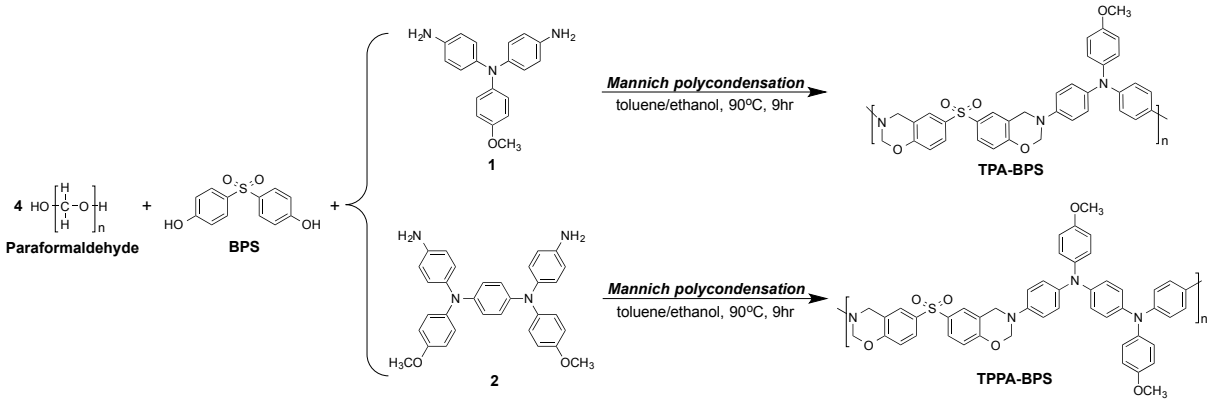
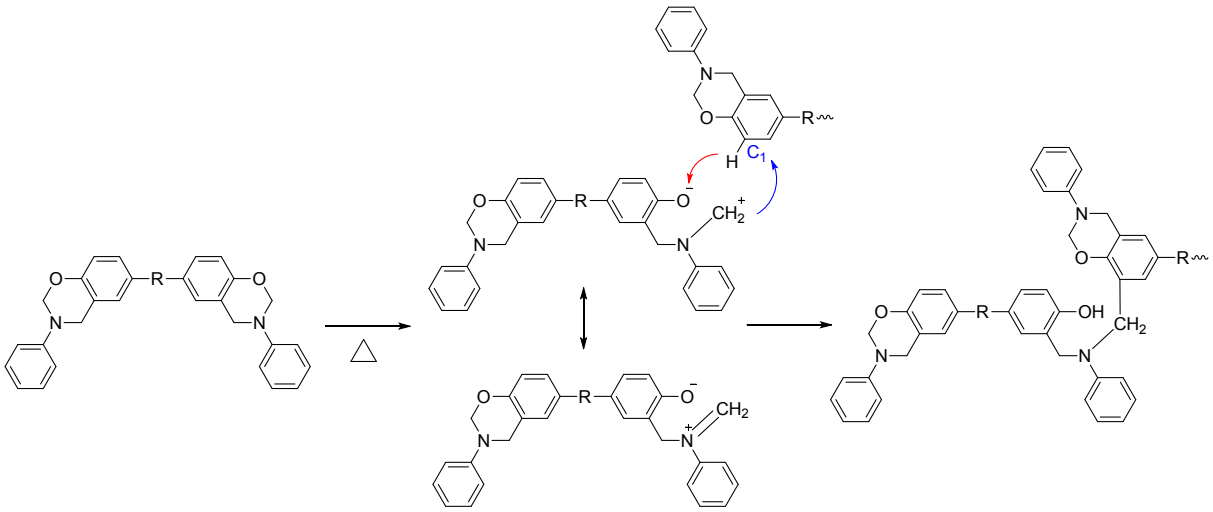


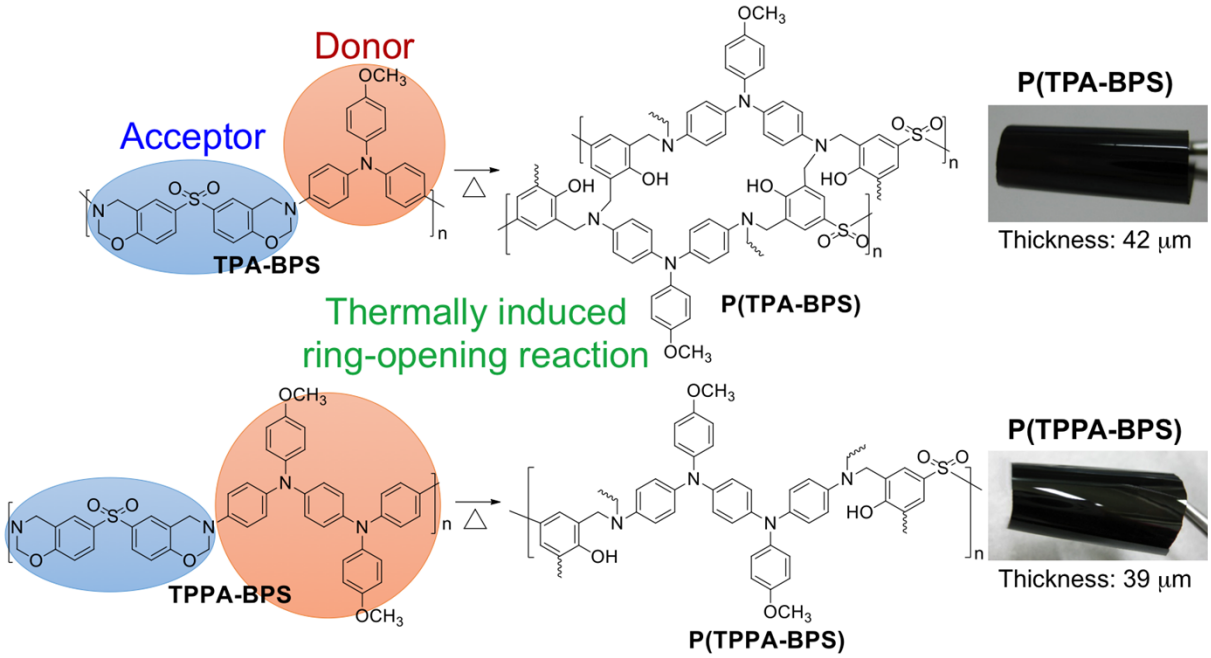
Fig. S6 *I-V* diagrams under repeating cycle tests of representative memory devices: (a) **TPA-BPS**, (b) **TPPA-BPS**, (c) **P(TPA-BPS)**, and (d) **P(TPPA-BPS)**.



Scheme S1. Synthesis of the polybenzoxazine precursors.



Scheme S2. Thermal ring opening polymerization mechanism of benzoxazines.



Scheme S3. The formation of intramolecular hydrogen bonds and increased intramolecular CT ways of PBs containing BPS.

Table S1. Inherent Viscosity[a] and Molecular Weight[b] of Polybenzoxazine Precursors

Sample Name	η_{inh} (dL/g)[a]	M_w	M_n	PDI
TPA-BPS	0.11	9.2×10^4	5.9×10^4	1.56
TPPA-BPS	0.12	8.5×10^4	5.0×10^4	1.72

[a] Measured at a polymer concentration of 0.5 g/dL in *N*-Methyl-2-pyrrolidone (NMP) at 30 °C.
[b] Calibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 0.5 mL/min at 40 °C.
[c] Polydispersity Index = M_w/M_n.
[d] Degree of Polymerization.

Table S2. Thermal Properties of Polybenzoxazines, **P(TPA-BPS)** and **P(TPPA-BPS)**.

Polymer	T_g (°C)[a]	CTE (ppm/°C)[b]	T_g (°C)[c]	T_d^5 (°C)[d]		T_d^{10} (°C)[d]		R_{w800} (%)[e]	LOI[f]
				Air	N_2	Air	N_2		
P(TPA-BPS)	284	60	290	350	350	405	395	57	40
P(TPPA-BPS)	298	54	310	410	395	440	435	57	40

[a.] Glass transition measured by TMA using the film/fiber mode with a constant applied load of 50 mN at a heating rate of 10 °C/min.

[b.] Coefficient of linear thermal expansion between 50 °C and 200 °C measured by TMA using the film/fiber mode with a constant applied load of 50 mN at a heating rate of 10 °C/min.

[c.] Glass transition measured by DMA using the film/fiber at a heating rate of 3 °C/min.

[d.] Temperature at which 5 % and 10 % weight loss occurred, respectively, recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 20 cm^3/min.

[e.] Residual weight percentages at 800 °C under nitrogen flow.

[f.] LOI = Limiting Oxygen Index = (17.5+0.4 ×char yield) at 800 °C.

Notes and references

1. (a) C. W. Chang, G. S. Liou and S. H. Hsiao, *J. Mater. Chem.*, 2007, **17**, 1007; (h) H. J. Yen and G. S. Liou, *Chem. Mater.*, 2009, **21**, 4062.
2. X. Y. Wang, F. Chen and Y. Gu, *Journal of Polymer Science: Part A: Polymer Chemistry*, 2011, **49**, 1443.