Supporting Information

Structural Effect on the Resistive Switching Behavior of Triphenylamine-Based Poly(azomethine)s

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1. Experimental

General: All chemicals were purchased from Aldrich (Shanghai, China) and used as received without further purification. Organic solvents were purified, dried and distilled under dry nitrogen. Weight-average (M_w) and number-average (M_n) molecular weights were determined by a waters 2690 gel permeation chromatography (GPC) using polystyrene standards eluted with tetrahydrofuran (THF, 1 mL/min). Fourier transform infrared (FTIR) spectra were obtained with a Thermo Nicolet 6700 FTIR spectrophotometer by dispersing the samples in KBr pellets. The ¹H nuclear magnetic resonance (¹H NMR) spectra were carried out at 400 MHz on a Bruker 400 AVANCE III spectrometer with dimethyl sulfoxide- d_6 (DMSO- d_6) as solvent. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer Diamond TG/DTA instrument at a heating rate of 10 °C/min under nitrogen atmosphere with a flow rate of 50 mL/min. UV-Visible absorption spectra of the linear and hyperbranched PAMs were obtained in toluene solution on a Perkin lambda 950 spectrophotometer. Cyclic voltammetry (CV) measurements were measured in an electrolyte solution of tetrabutylammonium perchlorate (*n*-Bu₄NClO₄) in acetonitrile (0.1 M) under an argon atmosphere, using platinum gauze and Ag/AgCl as the counter and reference electrodes respectively. A scan rate of 50 mV/s was used during the CV measurements.

Synthesis of Monomers and Polymers: Monomers of 4,4'-diamino-triphenylamine and 4,4',4''-triamino-triphenylamine were synthesized according to Ref 1.¹ The linear and hyperbranched PAMs were obtained through the polycondensation of the amine

with excessive aldehydes in ultrapure nitrogen atmosphere according to the reported method.² The synthesis routes are shown in **Scheme S1**. The M_n and polydispersity indexes of the linear and hyperbranched PAMs are $5.1 \times 10^3/1.87$ and $3.6 \times 10^3/1.03$, respectively.

Device Fabrication and Characterization: The resistive switching behaviors of the two PAMs were examined in the Ta/PAM/Pt capacitor-like structures. The Pt/Ti/SiO₂/Si substrates were pre-cleaned in the ethanol, acetone and isopropanol in an ultrasonic bath, each for 30 min in that order. Linear and hyperbranched PAM solutions of 6 mg/mL were prepared by dissolving the polymer powders in mixed solvents of 50:50 (*v:v*) tetrahydrofuran and cyclohexanone. The as-prepared PAM solutions were filtrated through polytetrafluoroethylene (PTFE) membrance micro-filters with a pore size of 0.45 μ m to remove any dissolved particles. The PAM functioning layers were deposited by spin-casting 50 μ L solutions of the polymers onto the pre-cleaned Pt/Ti/SiO₂/Si substrate at a spinning speed of 600 rpm for 15 s and then at 1000 rpm for 50 s, followed by being vacuum-dried at 80 °C overnight.

2. Calculation of Optical Band Gaps and Molecular Orbital Energy Levels:

The optical bandgap of the polymers can be calculated with the following equation:

$$E_{op} = hc / \lambda_{\text{onset}} \tag{1}$$

where *h* is the Plank constant ($6.63 \times 10^{-34} \text{ m}^2\text{kg/s}$), *c* is the speed of light ($3 \times 10^8 \text{ m/s}$), λ_{onset} is the absorption band edge of the polymer, and is 511 nm and 520 nm respectively for the linear and hyperbranched PAMs (**Fig. S3**).

The molecular orbital energy levels were derived from the cyclic voltammetry and E_{op} of the PAMs according to the following equations:

$$E_{HOMO} = - \left(E_{ox(onset)} + 4.8 - E_{FOC} \right) \tag{2}$$

$$E_{LUMO} = E_{HOMO} + E_{op} \tag{3}$$

where E_{HOMO} and E_{LUMO} correspond to the energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), $E_{ox(onset)}$ is the onset oxidation potential, 4.8 is the reference energy of ferrocene (FOC, 4.8 eV under the vacuum level), and E_{FOC} is the potential of FOC/FOC⁺ versus Ag/AgCl (0.38 eV, as measured by cyclic voltammetry). The onset oxidation potential of the linear and hyperbranched PAMs are 0.86 V and 0.90 V, respectively.

polymer	UV-Visible Absorption Spectra				Electrochemistr y	Energy level	
	λ^{a}	λ^{b}	λ_{onset}	E _{op}	Eox(onset)	НОМО	LUMO
Linear PAM	300 nm	447 nm	511 nm	2.43 eV	0.86 V	-5.28 eV	-2.85 eV
Hyperbranched PAM	289 nm	449 nm	520 nm	2.39 eV	0.90 V	-5.32 eV	-2.93 eV

Table S1. Optical absorption, electrochemistry and energy levels of the linear and hyperbranched PAMs

 λ^a and λ^b are the wavelengths of the absorption peaks at the shorter wavelength and longer wavelength regions, respectively.

3. Weibull distribution:

Weibull distribution component has been used to evaluate the uniformity of the resistive switching parameters of the PAM devices:

$$F(x) = 1 - \exp(-(x/x_0)^k)$$
(4)

where x and x_0 are random variable and scale parameter of the distribution of x, respectively. *k* and F are Weibull exponent and the cumulative probability for finding the random variable blew x relative to a scale parameter x_0 . The Weibull exponent can also be correlated with the standard deviation to mean ratio (Δ/μ) using the following equation:

$$\Delta/\mu = \frac{\left[\Gamma(1+2/k) - \Gamma^2(1+1/k)\right]^{1/2}}{\Gamma(1+1/k)}$$

(5) where Γ is the Gamma function.



Scheme S1. Synthesis route of the linear and hyperbranched PAMs.



Figure S1. FTIR spectra of the (a) linear and (b) hyperbranched PAMs.

In FTIR spectra, the absorption peak at 1618 cm⁻¹ and 1583 cm⁻¹ are ascribed to the formation of the C=N group. The absorption peak at 1693 cm⁻¹ is arising from the H-C=O moieties. The absorption peaks at 1315 cm⁻¹ and 1279 cm⁻¹ for the linear PAM as well as 1321 cm⁻¹ and 1303 cm⁻¹ for the hyperbranched PAM can be attributed to be the C-N group.



Figure S2. GPC traces of the linear and hyperbranched PAMs.



Figure S3. UV-Visible absorption spectra of the linear (red) and hyperbranched (blue) PAMs in toluene solutions.



Figure S4. TGA curves of the (a) linear and (b) hyperbranched PAMs.



Figure S5. Cyclic voltammogram of the linear (red) and hyperbranched (blue) PAMs.



Figure S6. Forming processes of the Ta/PAMs/Pt memory devices based on the (a) linear and (b) hyperbranched PAMs.



Figure S7. Pulse operations of the Ta/PAMs/Pt memory devices based on the (a) linear and (b) hyperbranched PAMs.



Figure S8. Retention time of the Ta/PAMs/Pt memory devices based on the (a) linear and (b) hyperbranched PAMs.



Figure S9. Top view scanning Electron Microscopic (SEM) images of the (a) linear and (b) hyperbranched PAM thin films.



Figure S10. Cross-sectional view SEM images of the (a) linear and (b) hyperbranched PAM thin films.



Figure S11. High-resolution transmission Electron Microscopic (TEM) images of the (a) linear and (b) hyperbranched PAM thin films.



Figure S12. Weibull plots of the HRS and LRS resistances of the Ta/PAM/Pt memory devices. The colored circle is experimental data and the black line is Weibull fitting.

The device performance, the distribution of the device resistances in its HRS and LRS in the present study, can also be evaluated with another important expression of the Weibull distribution³:

$$W(x) = \beta \operatorname{Ln}(X/X_{63\%}) \tag{6}$$

where X is the device resistance, β and X_{63%} are the shape factor (Weibull slope) and scale factor, respectively. The W(x) of the Ta/PAM/Pt memory device are plotted as a function of the Ln(HRS) and Ln(LRS), as shown in **Figure S12**. Obviously, the hyperbranched PAM devices exhibit more uniform distribution of both the HRS and LRS resistances.

References

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