Electronic Supplementary Information for

Different Resistive Switching Properties in D-A Polyazothines Based on Triphenylamine, Oxadiazole and 3,3'-dinitro-diphenylsulfone Moieties

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Calculation of molecular orbital energy levels and energy band gap of PAs:

$$E_g = \frac{hc}{\lambda_{onset}} \qquad \text{(S1)}$$

$$E_{HOMO} = -(E_{onset}(OX) + 4.8 - E_{FOC}) \qquad \text{(S2)}$$

$$E_{LUMO} = -(E_{onset}(RED) + 4.8 - E_{FOC}) \qquad \text{(S3)}$$

$$E_{LUMO} = E_{HOMO} + E_g \qquad \text{(S4)}$$

where E_g is the optical band gap of the polymers, h is the Planck constant (6.63×10^{-34} m^2kg/s), c is the speed of light (3×10^8 m/s), λ_{onset} is the onset optical absorbance wavelength of the polymers, E_{HOMO} and E_{LUMO} are the HOMO and LUMO energy levels, $E_{onset}(OX)$ is the onset oxidation potential of the polymers, $E_{onset}(RED)$ is the onset reduction potential of the polymers, 4.8 is the reference energy level of ferrocene (FOC, 4.8 eV below the vacuum level) and E_{FOC} is the potential of FOC/FOC$^+$ vs. Ag/AgCl (0.38 eV, as measured by cyclic voltammetry). Based on the $E_{onset}(OX)$ and λ_{onset} of PA-1, the HOMO level and optical band gap are calculated to be -5.05 eV and 2.88 eV, respectively, according to **Equations S1** and **S2**. Therefore, the LUMO level of PA-1 is deduced to be -2.17 eV with **Equation S4**. Here, the optical energy band gap is used to calculate the LUMO level. However, as PA-1 also exhibits reduction peak in the cyclic voltammetry (CV) measurements, the LUMO level can be obtained from the electrochemical data directly by using **Equation S3**, which is -3.62 eV and close to our previous value. The corresponding energy band gap of PA-1 is then 1.43 eV and much different from 2.88 eV of the optical band gap. It is a common sense that the optical band gap of a polymeric material is different

from its energy band gap.[1,2] Also, as the molecular simulation of the basic unit (BU) of the polymer does not consider the effect of π conjugation of the macromolecule chains, the simulated energy levels of the BU, in particular the LUMO level, usually shows some deviation from the experimental value.[3,4] On the other hand, as PA-2 only exhibits reduction behavior in the CV profile, the LUMO level (-3.57 eV) has to be calculated using **Equation S3** with its $E_{onset}(RED)$ of -0.85 V. With the optical band gap of 3.13 eV as derived from the onset optical absorbance wavelength of 397 nm from **Equation S1**, PA-2 shows a HOMO level of -6.70 eV as deduced from **Equation S4**.
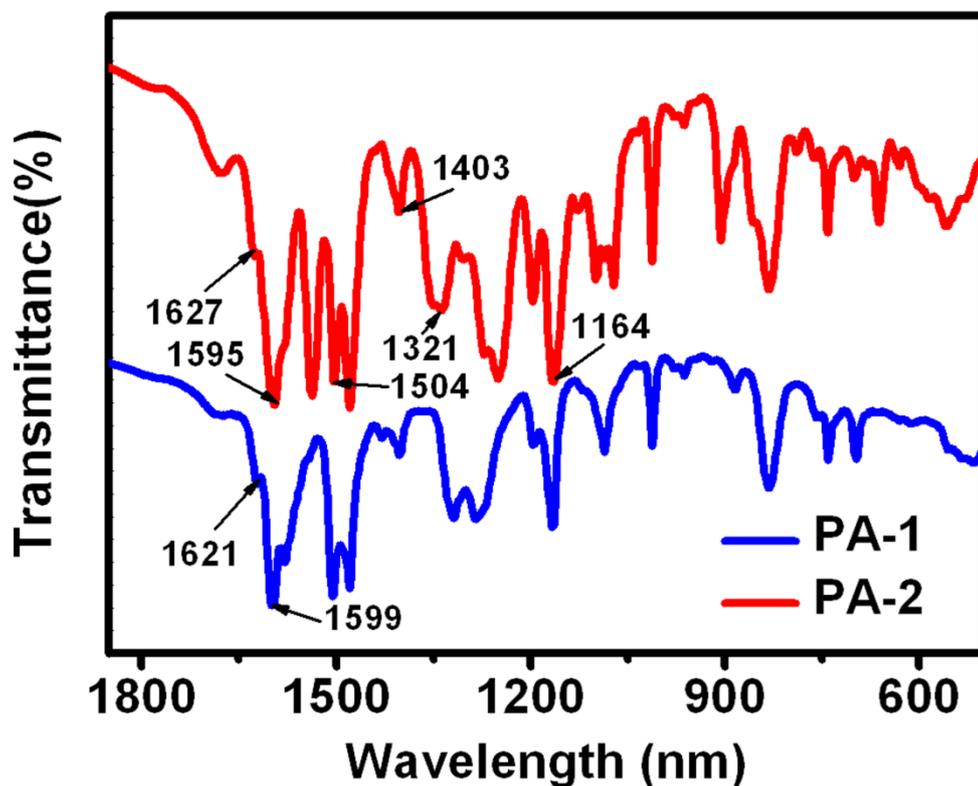
Figure S1 FT-IR spectra of PA-1 and PA-2.

The diamine monomer M1 was synthesized by the nucleophilic reaction between p-aminothiophenol and 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole with a yield of 76.8%. Similarly, the dialdehyde monomer, bis-(3-nitro-4-p-formylphenyloxy-phenyl) sulfone, was synthesized with a yield of 81.2%. As shown in Scheme 1, the two poly(schiff base)s were obtained by polycondensation of M1 and the corresponding dialdehyde monomers. The chemical structures of the PAs were confirmed by 1H NMR and FT-IR spectra. The weak absorption peaks at 1621 cm^{-1} and 1627 cm^{-1} are the characteristic signals of C=N stretching in the oxadiazole unities. The peaks at around 1599 cm^{-1} and 1595 cm^{-1} are attributed to the vibrating stretching of C=N in the imine moieties of the as-synthesized scihff bases. The characteristic magnetic

resonance signals of the CH=N moieties are observed with the chemical shifts of

10.14 ppm and 10.10 ppm, respectively, in the 1H NMR spectra of the PAs. Both PAs

exhibit good room-temperature solubility in common solvent, such as cyclohexanone,

DMF and NMP, and the inherent viscosity of PA-1 and PA-2 are 0.45 and 0.51 dL/g
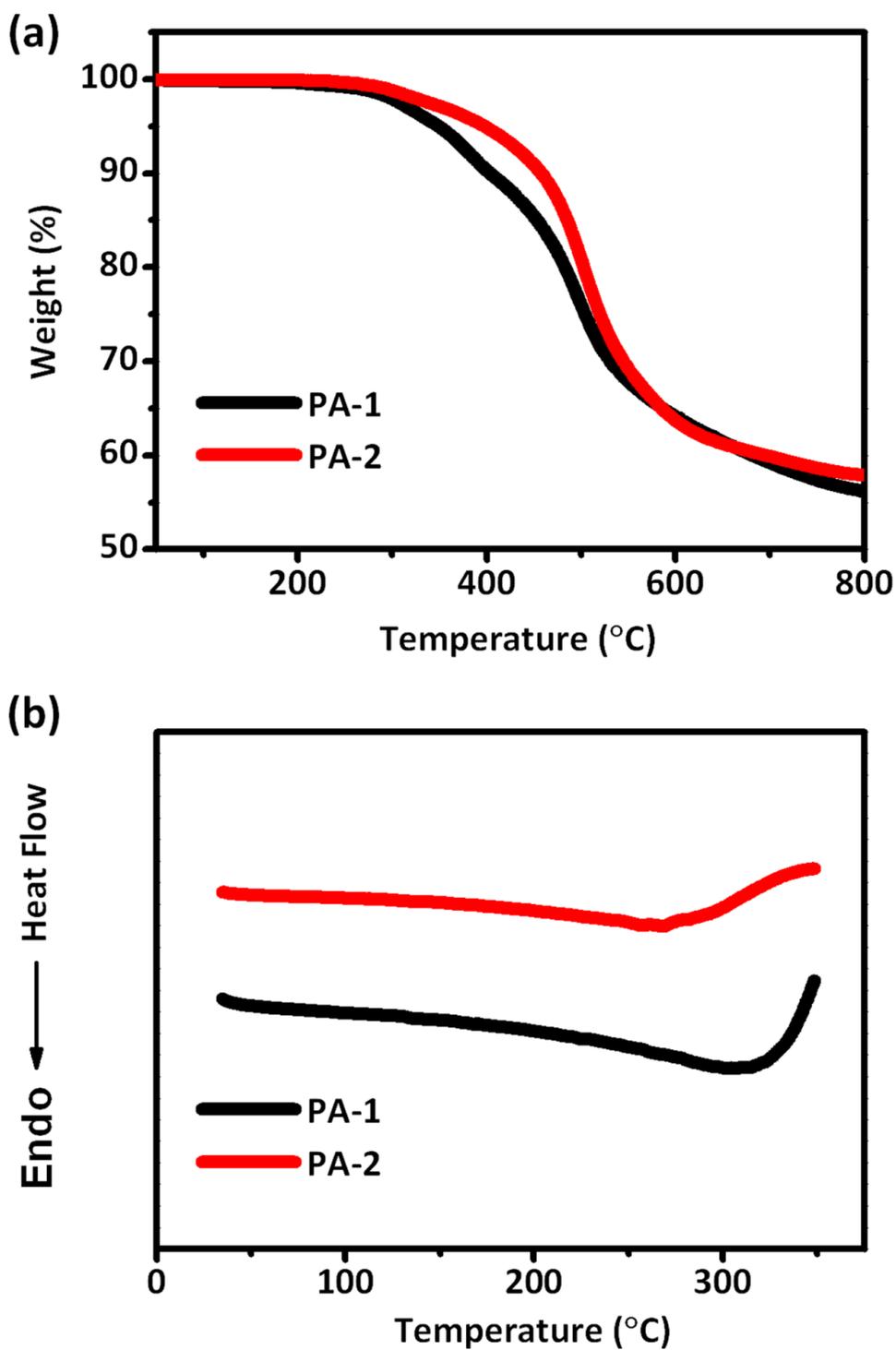
in NMP, respectively.

Figure S2 (a) TGA and (b) DSC curves of PA-1 and PA-2 in nitrogen.

The thermal properties of the PAs were evaluated by DSC and TGA analysis as

shown in Figure S2. The onset thermal degradation temperatures ($T_d(10\%)$) and glass

transition temperatures (T_g) of PA-1 and PA-2 are 404 °C/326 °C and 458 °C/279 °C,

respectively. The T_g of PA-1 is higher than that of PA-2, and is in accordance with the fact that the molecular size of the PA-1 dialdehyde moiety is larger than that of PA-2 dialdehyde moiety. The good solubility and moderate viscosity of both polymers promise them excellent solution processability for easy device fabrication, while the thermal stability of either PA-1 or PA-2 is highly desired for achieving high endurance of the polymer electronic devices.
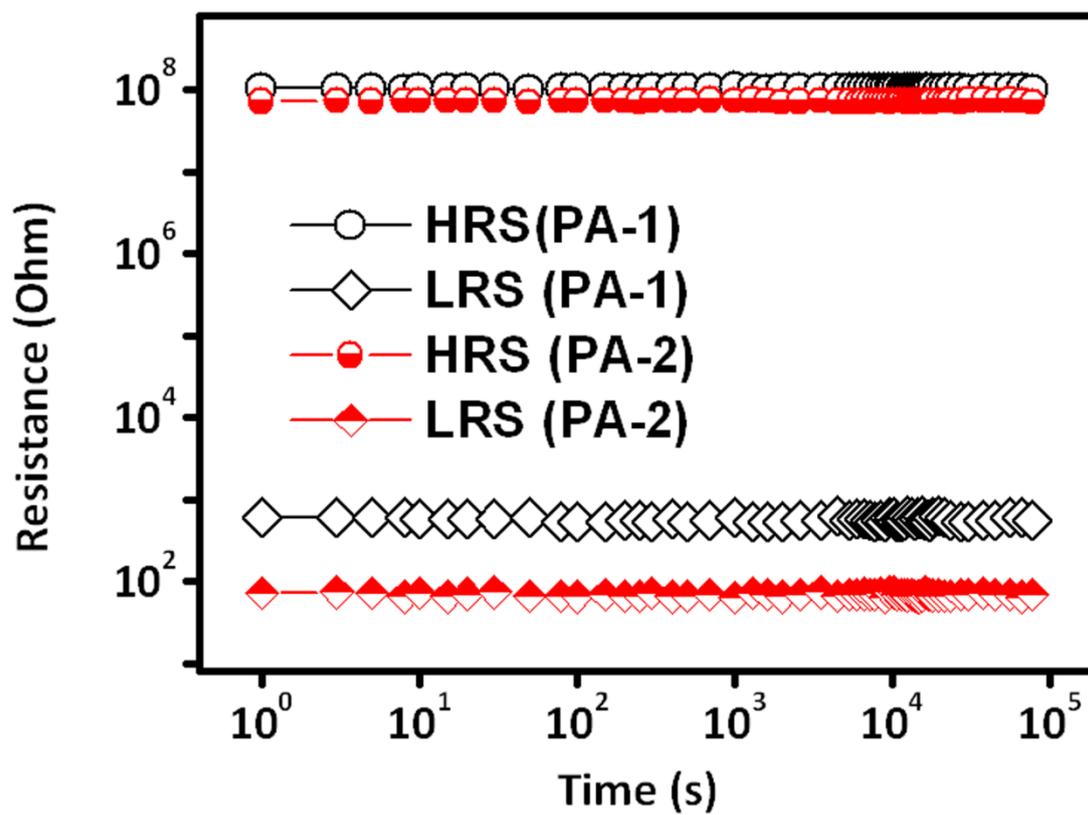
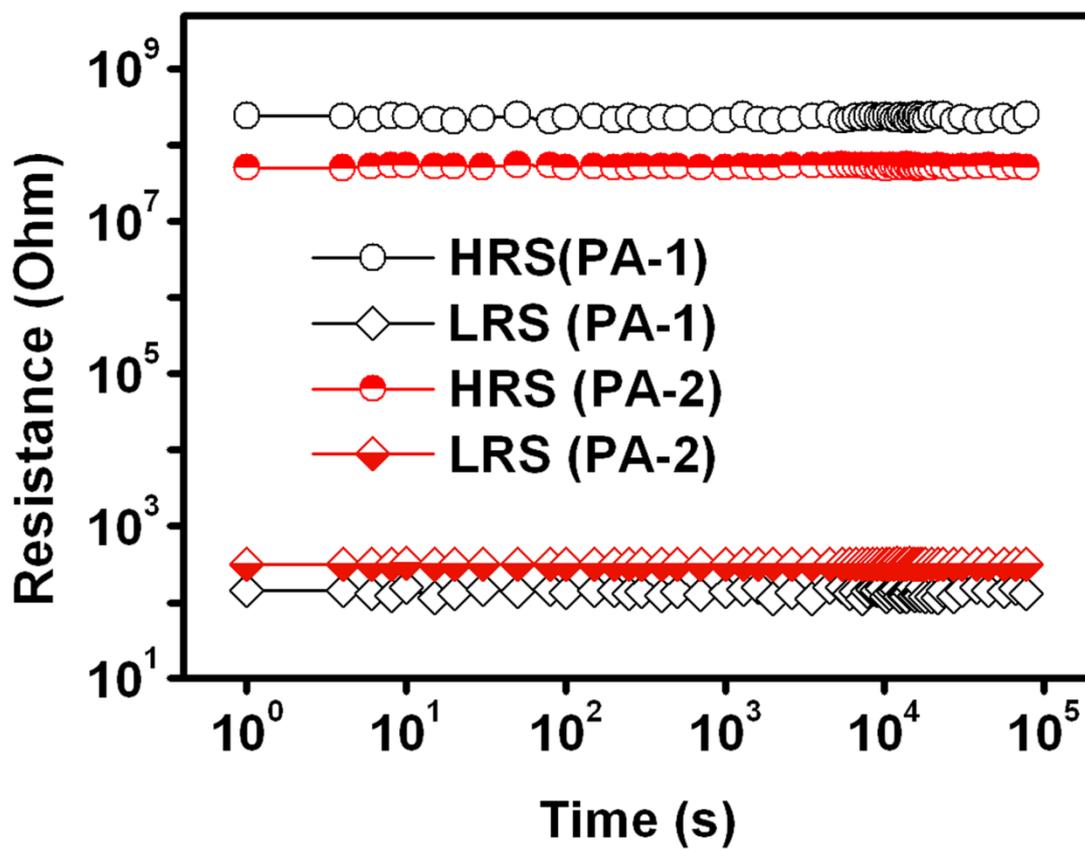**Figure S3** Retention performance of the Pt/PAs/Pt devices.

Figure S4 Retention performance of the Al/PAs/Pt devices.

References

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