

A salification-induced charge transfer effect for improving the resistive memory performance of azo derivative-based devices

Quan Liu,^a Qingfeng Xu,^a Huilong Dong,^b Hua Li,^a Dongyun Chen,^a Lihua Wang,^a Youyong Li^b and Jianmei Lu^{*a}

Supporting Information

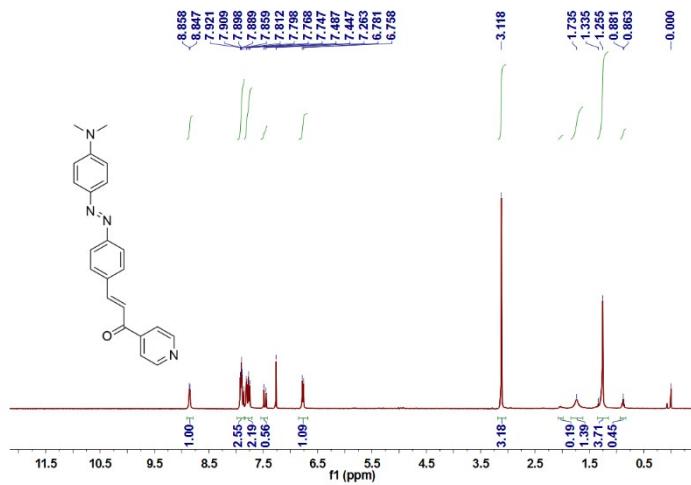


Figure S1. The ^1H NMR spectra of AZOCP in CDCl_3 .

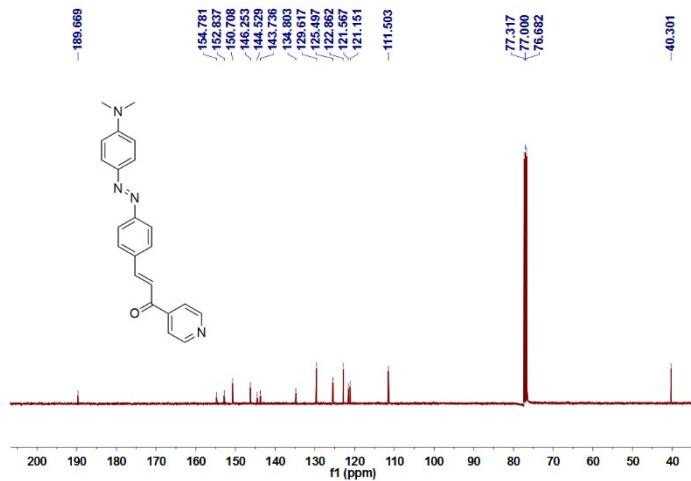


Figure S2. The ^{13}C NMR spectra of **AZOCP** in CDCl_3 .

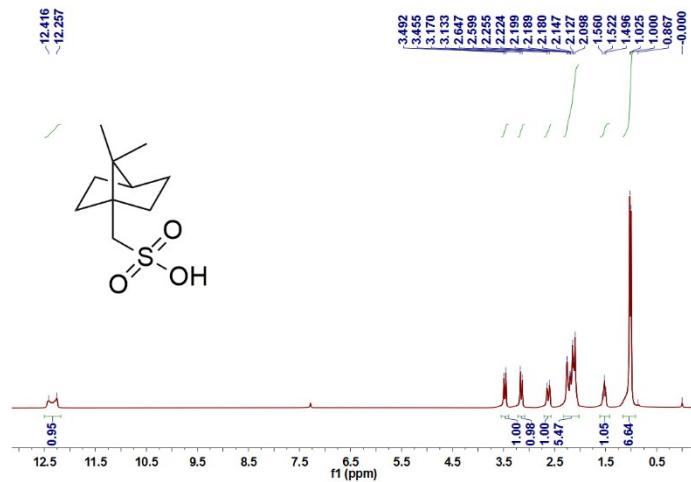


Figure S3. The ^1H NMR spectra of CSA in CDCl_3 .

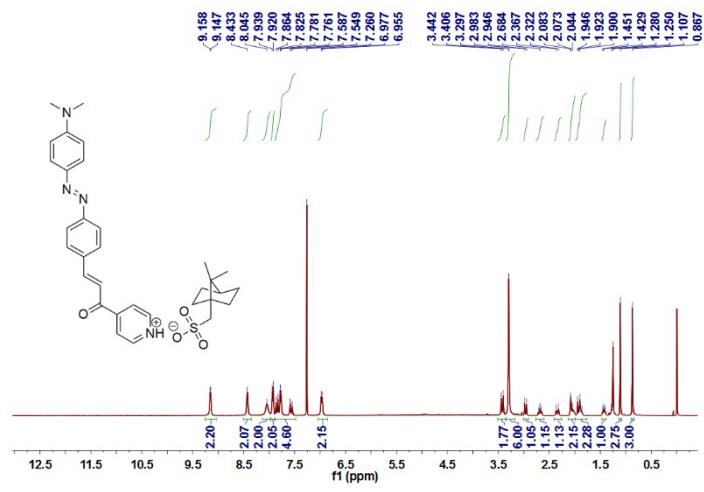


Figure S4. The ^1H NMR spectra of **AZOCP-CSA** in CDCl_3 .

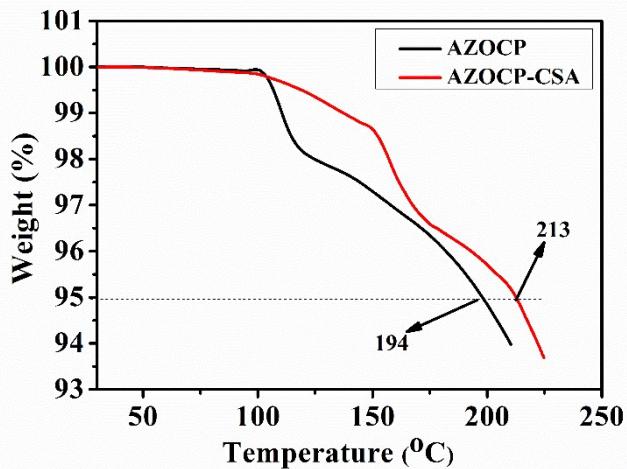
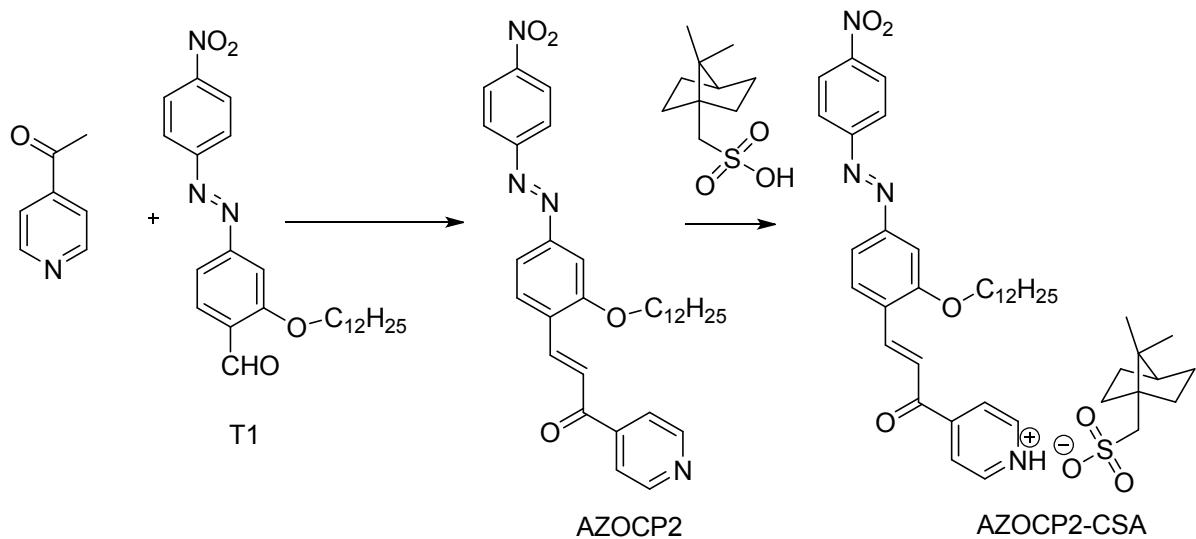


Figure S5. Thermogravimetric analysis (TGA) curves of **AZOCP** and **AZOCP-CSA** with a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ under a nitrogen atmosphere.



Scheme S1 The synthetic routes and molecular structures of **AZOCP2** and **AZOCP2-CSA**.

Synthesis of 2-(dodecyloxy)-4-((4-nitrophenyl)diazenyl)benzaldehyde (T1)

¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.57 (s, 1H, CHO), 8.48 (d, J = 3.2 Hz, 1H, ArH), 8.38 (d, J = 11.6 Hz, 2H, ArH), 8.20 (dd, J = 12.0 Hz, J = 3.6 Hz, 1H, ArH), 8.02 (d, J = 12.0 Hz, 2H, ArH), 7.15 (d, J = 11.6 Hz, 1H, ArH), 4.22 (m, 2H, CH₂), 1.92 (m, 2H, CH₂), 1.41 (m, 18H, CH₂), 0.88 (t, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ (ppm): 189.1 (C=O), 164.2 (ArC), 155.6 (ArC), 148.6 (ArC), 146.1 (ArC), 130.5 (ArC), 125.2 (ArC), 124.8 (ArC), 124.1 (ArC), 123.4 (ArC), 113.0 (ArC), 69.4 (CH₂), 31.9 (CH₂), 29.63 (CH₂), 29.61 (CH₂), 29.56 (CH₂), 29.52 (CH₂), 29.34 (CH₂), 29.30 (CH₂), 29.0 (CH₂), 26.0 (CH₂), 22.7 (CH₂), 14.1 (CH₃). HRMS: calcd for C₂₅H₃₃N₃O₄ [M + H]⁺ 440.2549, found 440.2552.

Synthesis of 3-(2-dodecyloxy)-4-((4-nitrophenyl)diazenyl)phenyl)-1-(pyridin-4-yl)prop-2-en-1-one (AZOCP2)

¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.81 (m, 1H, ArH), 8.58 (m, 1H, ArH), 8.24 (m, 3H, ArH), 7.60 (m, , 6H, ArH), 6.86 (s, 2H, ArH), 4.12 (m, 2H, CH₂), 2.02 (m, 2H, CH₂), 1.38 (m, 18H, CH₂), 0.88 (t, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ (ppm): 192.7 (C=O), 159.9 (ArC), 159.4 (ArC), 155.6 (ArC), 150.4 (ArC), 148.2 (ArC), 146.2 (ArC), 135.4 (ArC), 129.2 (ArC), 124.7 (ArC), 124.6 (ArC), 123.1 (ArC), 120.1 (ArC), 112.2 (ArC), 111.4 (ArC), 91.3 (CH=CH), 69.5 (CH₂), 31.9 (CH₂), 29.8 (CH₂), 29.7 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.0 (CH₂), 26.1 (CH₂), 22.7 (CH₂), 14.1 (CH₃). HRMS: calcd for C₃₂H₃₈N₄O₄ [M + H]⁺ 543.2971, found 543.2481.

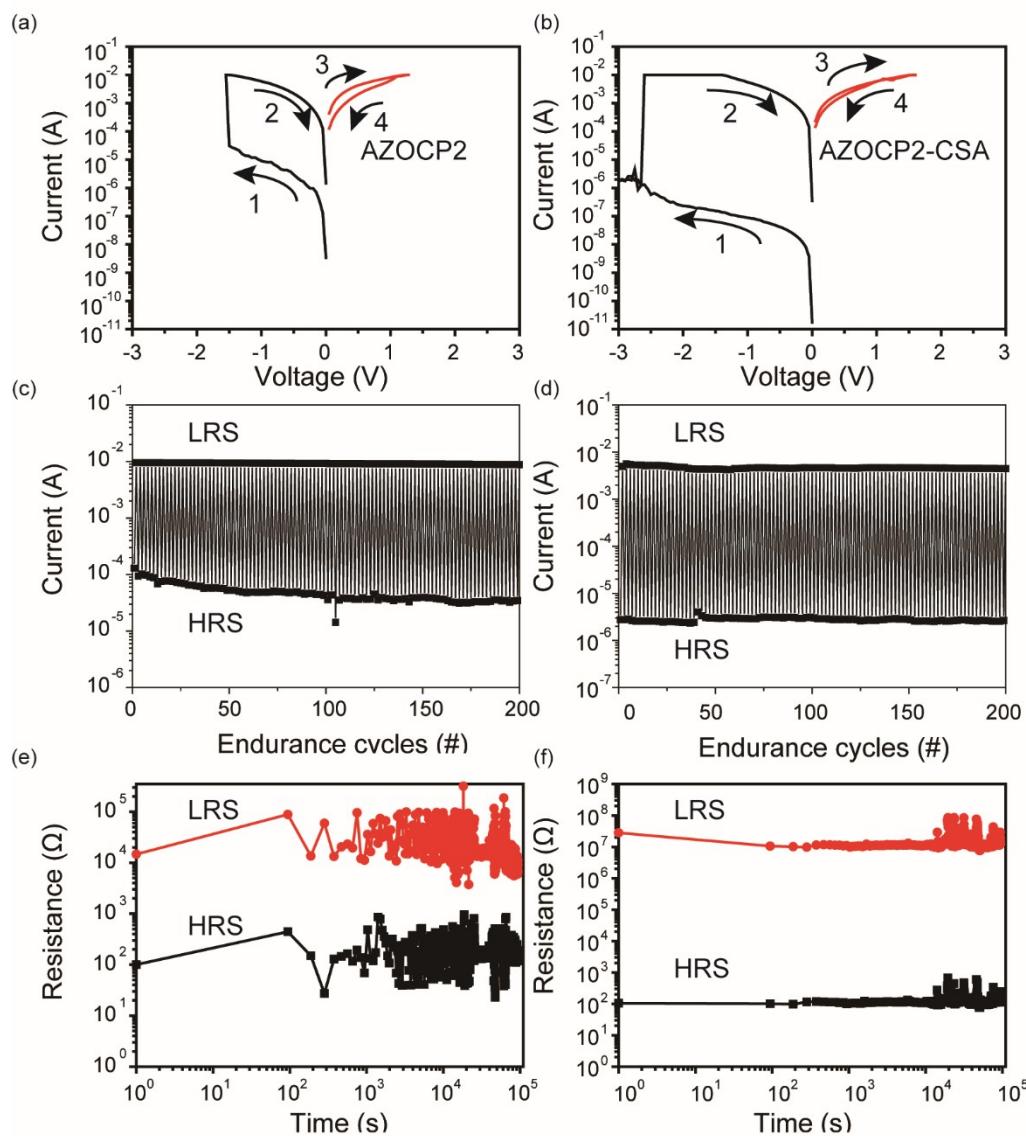


Figure S6 Current–voltage (I–V) characteristics of Au/AZOCP2/ITO and Au/AZOCP2-CSA/ITO memory device(a and b); the endurance cycles of Au/ AZOCP2/ITO and Au/AZOCP2-CSA /ITO memory device under a constant stress of -1.0 V (c and d) and the effect of retention time (e and f).

Table S1. The HOMO orbital, LUMO orbital and energy gap (E_{gap}) from DFT simulation result and experimental data of **AZOCP** and **AZOCP-CSA**.

	HOMO (eV) (simul)	LUMO (eV) (simul)	E_{gap} (eV) (simul)	HOMO (eV) (exper)	LUMO (eV) (exper)	E_{gap} (eV) (exper)
AZOCP	-4.76	-3.16	1.60	-5.24	-3.02	2.22
AZOCP-		-6.47	0.36	-5.30	-3.17	2.13
CSA	-6.83					