Electronic Supplementary Material (ESI) for Nanoscale.

Metal Complex Modified Azo Polymer for Multilevel Organic Memories

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1. Experimental Section

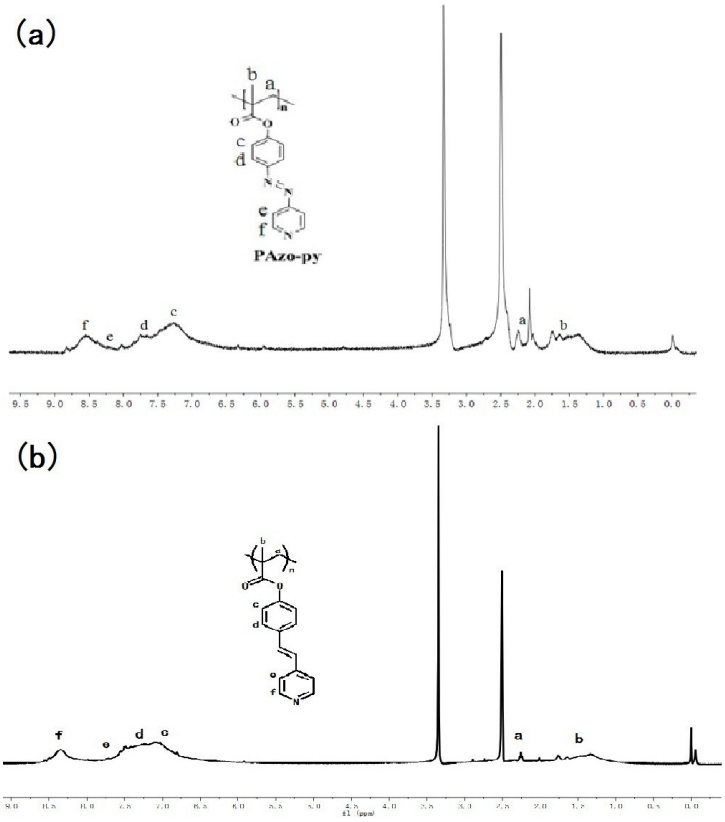


Figure S1 (a) ^{1}H NMR for PAzo-py ($CDCl_3$); (b) ^{1}H NMR for Pyvp ($CDCl_3$).

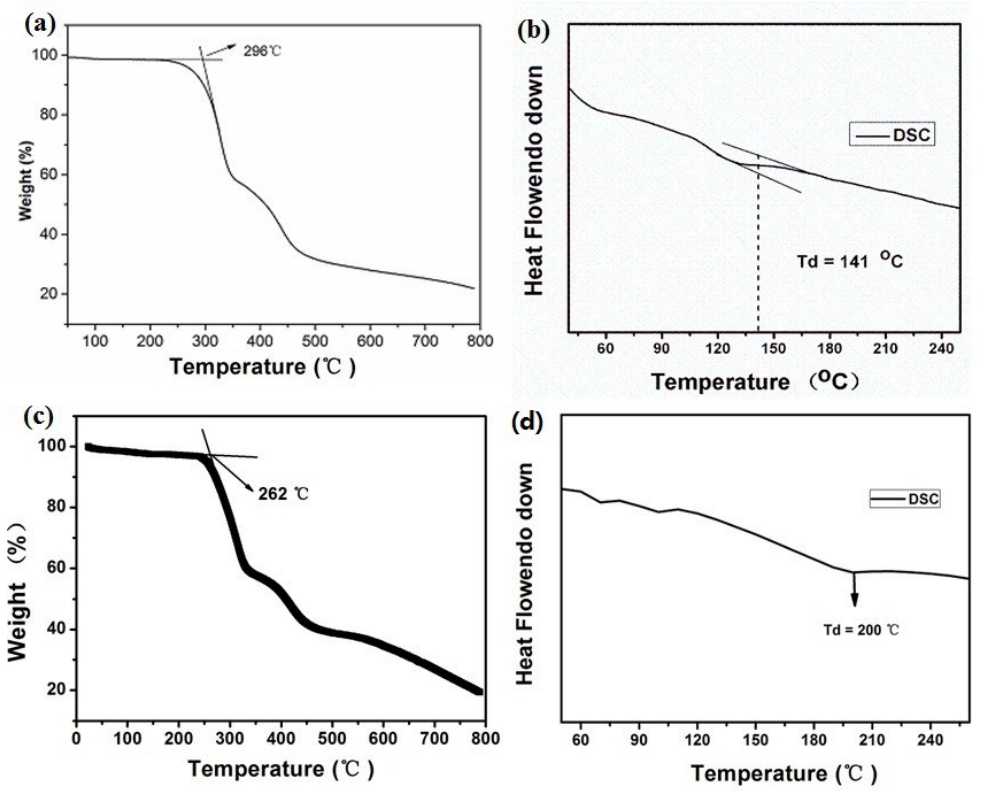
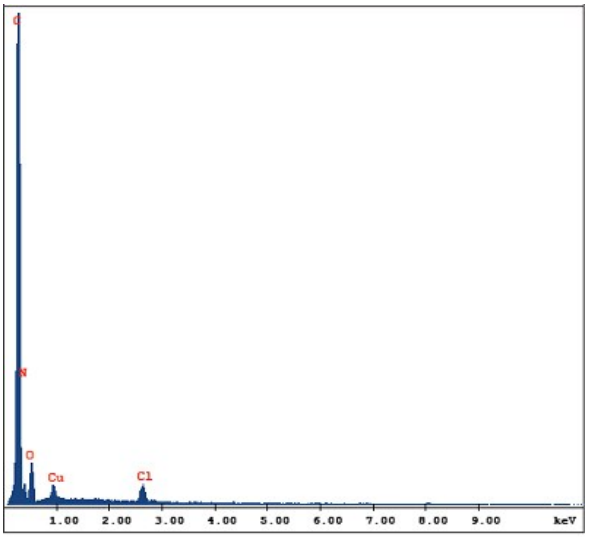


Figure S2 (a) TGA curves of PAzo-py under an air flow rate of 50 ml min^{-1} (heating rate: 10 °C min^{-1}); (b) DSC curves for PAzo-py; (c) TGA curves for PAzo-py-$Cu(Phen)Cl_2$; (d) DSC curves for PAzo-py-$Cu(Phen)Cl_2$.



Element	Wt %	At %
C K	75.45	80.90
N K	11.24	10.33
O K	9.69	7.80
CuL	2.18	0.44
ClK	1.44	0.52
Total	100.00	100.00

Figure S3a EDS for PAzo-py-$Cu(Phen)Cl_2$.

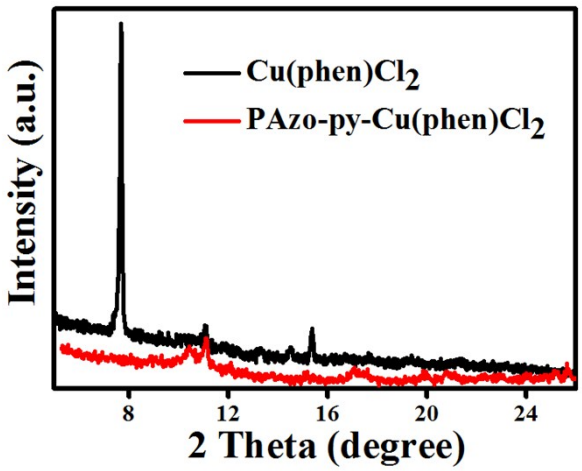


Figure S3b X−ray diffraction scans of $Cu(Phen)Cl_2$ and PAzo-py-$Cu(Phen)Cl_2$.

Table S1 The content of Cu^{2+} in PAzo-py-$Cu(Phen)Cl_2$ complexes determined by ICP-AES

Samples	the concentration of Cu^{2+} in two PAzo-py-$Cu(Phen)Cl_2$ composites
PAzo-py-$Cu(Phen)Cl_2$	2.0%
PAzo-py-$Cu(Phen)Cl_2$-a	3.0%

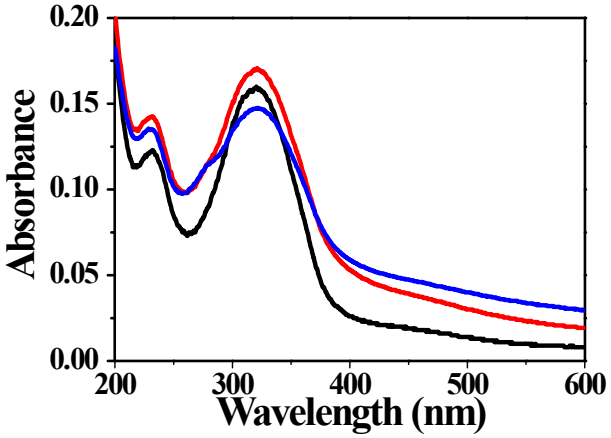


Figure S4 UV-vis spectra of the polymer films (black, PAzo-py; red, PAzo-py-$Cu(Phen)Cl_2$; blue, PAzo-py-$Cu(Phen)Cl_2$-a;

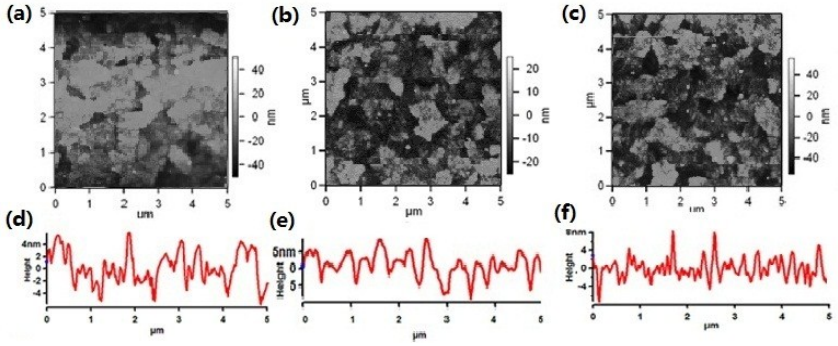


Figure S5 (a) AFM of PAzo-py film, roughness = 2.39 nm; (b) AFM of PAzo-py-Cu(Phen)Cl_2 film, roughness = 3.16 nm; (c) AFM of PAzo-py-Pd(Phen)Cl_2 film, roughness = 3.09 nm; (d) typical cross-section profile of AFM topographic image of PAzo-py film; (e) typical cross-section profile of AFM topographic image of PAzo-py-Cu(Phen)Cl_2 film; (f) typical cross-section profile of AFM topographic image of PAzo-py-Pd(Phen)Cl_2 film.

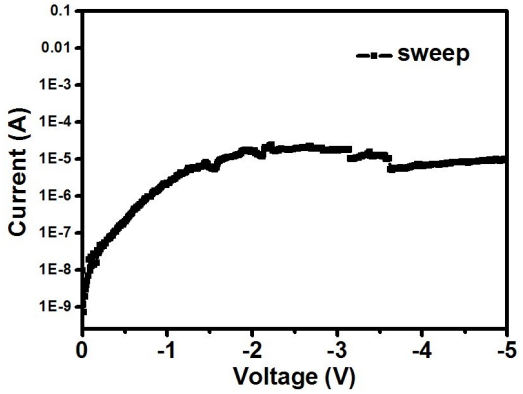


Figure S6 Current-voltage (I-V) characteristics of the memory device based on ITO/Pyvp/Al.

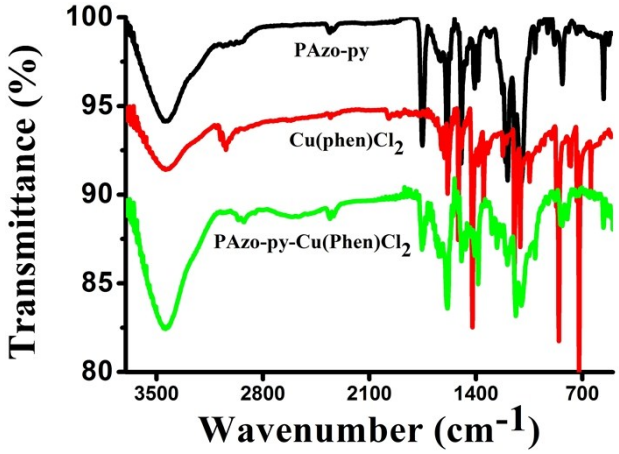


Figure S7 IR for PAzo-py, Cu(Phen)Cl_2 and PAzo-py-Cu(Phen)Cl_2 powder.

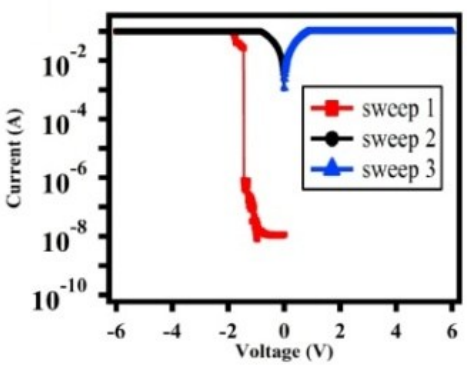


Figure S8 Current-voltage characteristics of device Au/PAzo-py /Au.

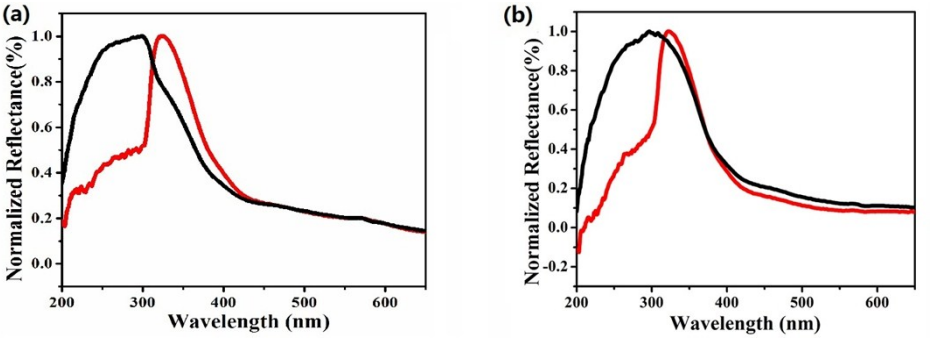


Figure S9 The diffusion reflectance UV-vis spectra for (a) PAzo-py-Cu(Phen)Cl_2 film (black, PAzo-py-Cu(Phen)Cl_2 film; red, PAzo-py-Cu(Phen)Cl_2 film under electrical field); (b) PAzo-py film (black, PAzo-py film; red, PAzo-py film under electrical field).

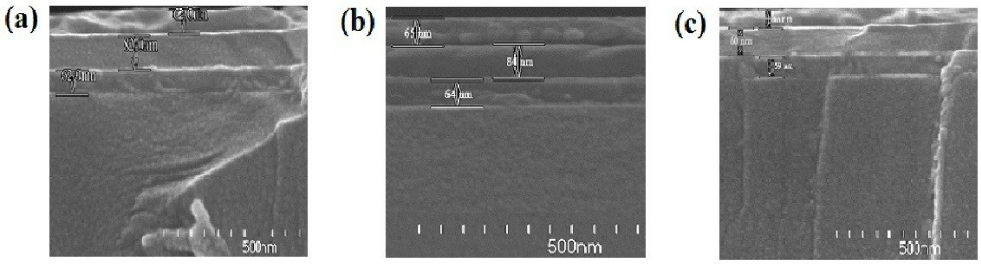


Figure S10 The cross section SEM image of the devices (a) ITO/PAzo-py/Al; (b) ITO/PAzo-py-Cu(Phen)Cl_2/Al; (c) ITO/PAzo-py-Pd(Phen)Cl_2/Al.

2. Computational details

Theoretical calculations are performed by DMol3 density-functional code.[1] The generalized gradient approximation[2] functional by B88 exchange[3] and LYP correlation[4] (GGA-BLYP), along with a double numerical plus polarization (DNP) basis set, is used in all calculations. Density functional semicore pseudopotential (DSPPs)[5] available in DMol3 is employed for core treatment of the azopy with Pd. For simplification, the polymer chain is represented by a butyl chain in our calculations.

1. (a) Delley, B., *J. Chem. Phys.* **1990,** 92, 508; (b) Delley, B., *J. Chem. Phys.* **2000,** 113, 7756.

2. Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996,** 77, 3865.

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