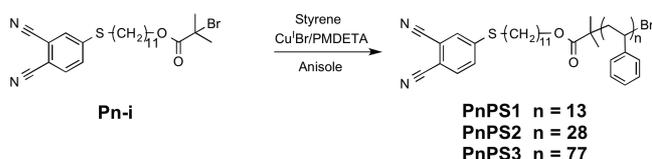


Supporting Information

Star Polymer with a Metallo-Phthalocyanine Core as a Tunable Charge Storage Material for Nonvolatile Transistor Memory

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Scheme S1. Synthesis of phthalonitrile-terminated polystyrene (**PnPS1-3**).



Synthesis of PnPS3: Pn-i (0.5 g, 1.04 mmol) and anisole (22.3 mL) were added to a dry Schlenk flask followed by styrene (S) (23.9 mL, 208.6 mmol). Then, CuBr (150 mg, 1.94 mmol) and PMDETA (218 μ L, 1.04 mmol) were added to the flask. The resulting mixture was degassed by three freeze-pump-thaw cycles. An initial sample was taken and the sealed flask was placed in an oil bath thermostated at 70 °C. The polymerization was monitored by GPC and ^1H NMR. The reaction was stopped after 22 h with 35% conversion by opening the flask and exposing the catalyst complex in the solution to air. The resulting polymer was purified by preparative recycling GPC to remove byproducts by radical-radical recombination and any catalysts. The molecular weight and polydispersity were estimated by analytical GPC, resulting a polymer **PnPS3** with $M_n = 8.5$ kg/mol and $M_w/M_n = 1.05$.

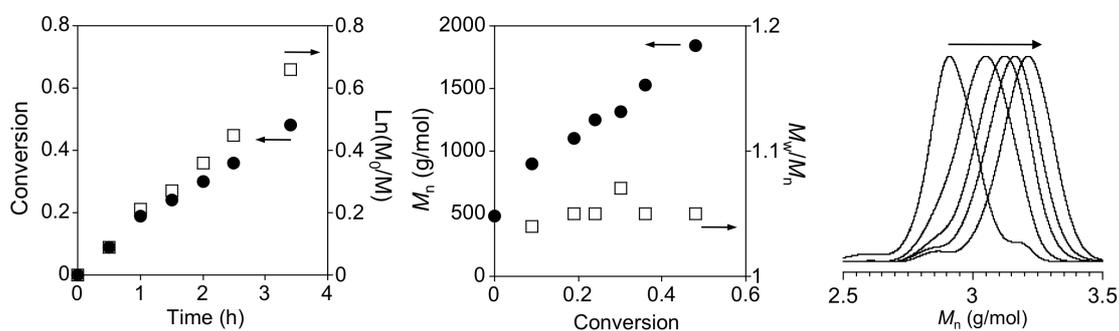
^1H NMR (400MHz) in CDCl_3 : δ 7.61 (d, $J = 8.0$ Hz, 1H; Pn-i ArH), 7.54 (d, $J = 2.0$ Hz, 1H; Pn-i ArH), 7.46 (dd, $J = 8.0, 1.6$ Hz, 1H; Pn-i ArH), 7.2–6.8 (br, mH; PS Ar-H), 6.8–6.0 (br, mH; PS Ar-H), 4.4 (br, 2H; OCH_2), 3.0 (t, 2H; SCH_2), 2.2–1.6 (br, mH, PS backbone CH), 1.6–0.8 (br, mH; PS backbone CH_2) ppm.

Table S1. Syntheses of **PnPS1-3** by ATRP.

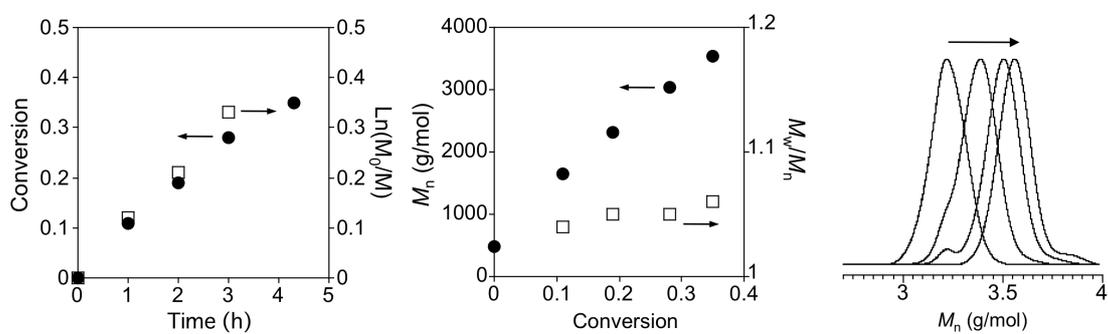
Polymer	Conditions [Pn-i]:[S]:[CuBr]:[PMDETA]	Time (h)	Conversion (%) ^a	M_n ^b (g/mol)	M_w/M_n ^b
PnPS1	1:20:0.2:0.2	3.5	50	1850	1.05
PnPS2	1:60:1:1	3	35	3360	1.03
PnPS3	1:200:1:1	22	35	8500	1.05

^aBased on GC analysis. ^bNumber-averaged molecular weights and polydispersities determined by GPC analysis based on polystyrene standards.

(a) **PnPS1**



(b) **PnPS2**



(c) **PnPS3**

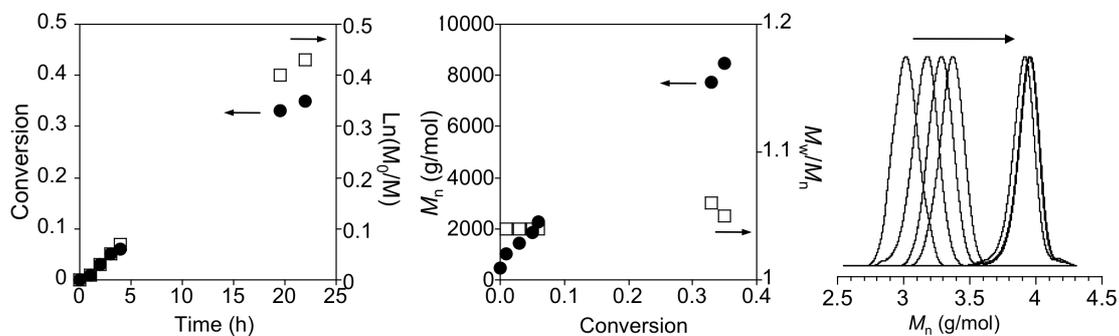
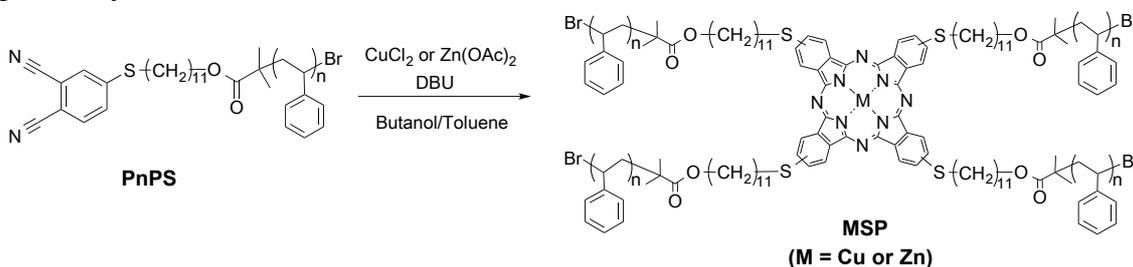


Figure S1. Kinetics, dependence of molecular weights and molecular weight distribution, and evolution of analytical GPC traces during synthesis of (a) **PnPS1**, (b) **PnPS2** and (c) **PnPS3** by ATRP.

Scheme S2. Synthesis of a star-shaped polystyrene with a Cu or Zn complex of a phthalocyanine core.



CuSP1, 3 and **ZnSP1-3** were synthesized by following procedures using **PnPS1-3**.

Synthesis of ZnSP1: **PnPS1** ($M_n = 1.85$ kg/mol; 0.3 g) was dissolved in the mixture of butanol (0.2 mL) and toluene (0.1 mL). Zinc acetate (17.8 mg, 81.0 μ mol) and DBU (12.2 μ L, 81.0 μ mol) were then added, and the reaction mixture was refluxed under Ar. The reaction was monitored by analytical GPC. The mixture was cooled to the room temperature after 12 hours and passed through alumina column to remove Cu catalyst. The residue was purified by preparative recycling GPC to remove unreacted **PnPS1**, giving **ZnSP1** as a green powder ($M_n = 6.90$ kg/mol, $M_w/M_n = 1.10$) in 40% yield.

Synthesis of CuSP1: **PnPS1** ($M_n = 1.85$ kg/mol; 0.5 g) was dissolved in the mixture of butanol (0.3 mL) and toluene (0.1 mL). Copper Chloride (3.8 mg, 28.0 μ mol) and DBU (4.2 μ L, 28.0 μ mol) were then added, and the reaction mixture was refluxed under Ar. The reaction was monitored by analytical GPC. The mixture was cooled to the room temperature after 12 hours and passed through alumina column to remove Cu catalyst. The residue was purified by preparative recycling GPC to remove unreacted **PnPS1**, giving **CuSP1** as a green powder ($M_n = 6.76$ kg/mol, $M_w/M_n = 1.05$) in 45% yield.

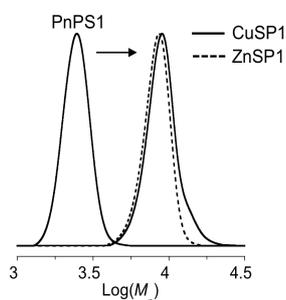


Figure S2. GPC profiles of **PnPS1**, **CuSP1** and **ZnSP1**.

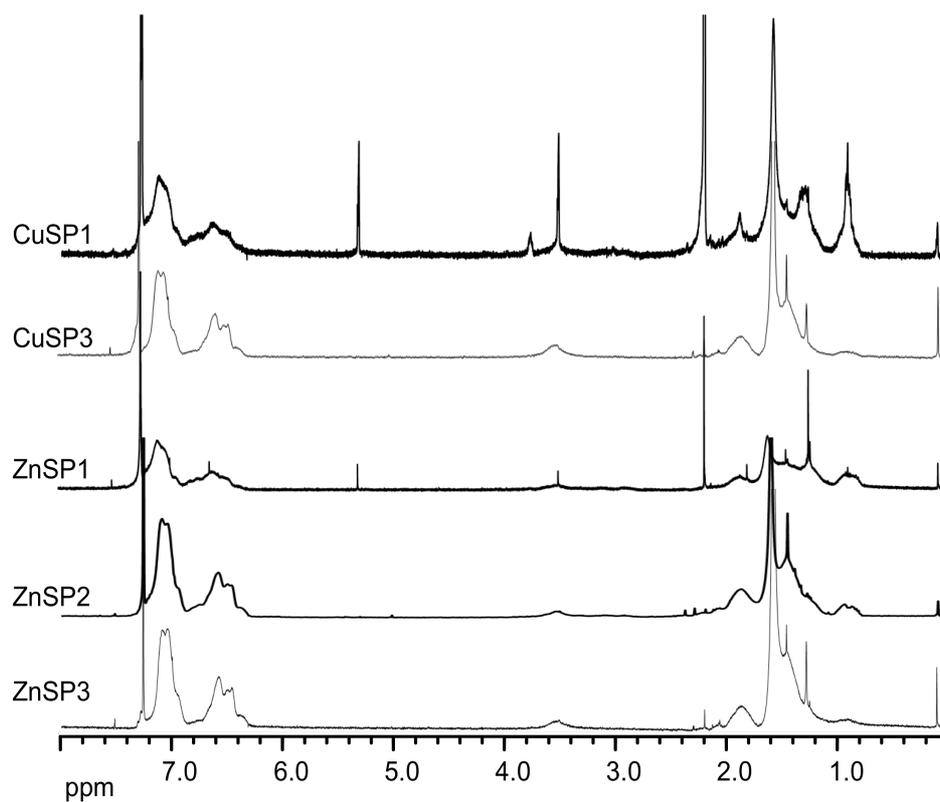


Figure S3. ^1H NMR of **CuPc** or **ZnPc**-cored star-shaped polystyrene in CDCl_3 .

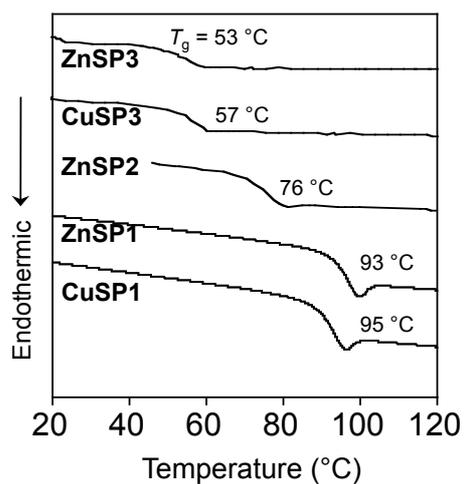


Figure S4. Glass transition temperatures of polymers in DSC of 2nd heating profiles with scanning rate of $10\text{ }^\circ\text{C min}^{-1}$.

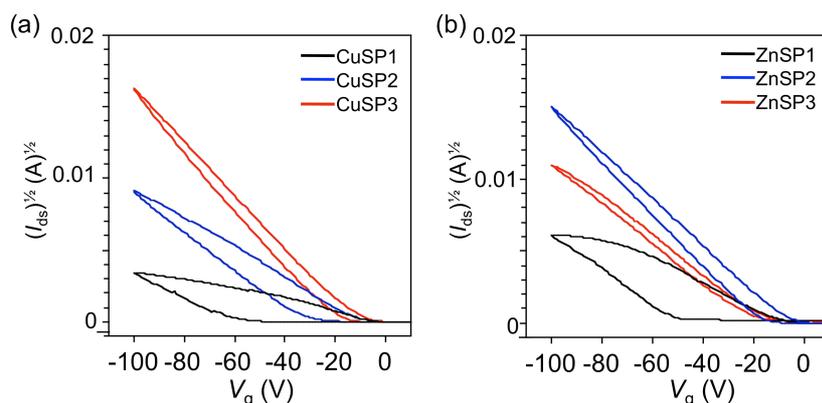


Figure S5. The linear plots of square root of drain-to-source current vs gate bias of pentacene-based OFET memory with (a) CuSP and (b) ZnSP as charge storage layers.

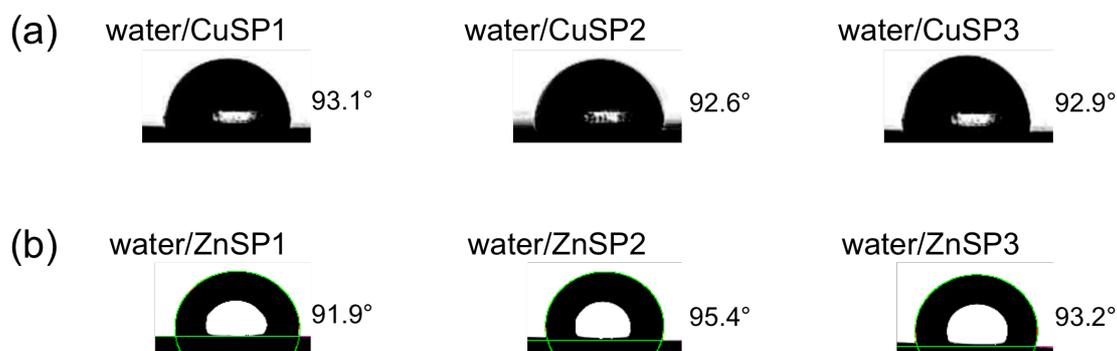


Figure S6. Contact angles of water droplet on **CuSP1-3** films (a) and **ZnSP1-3** (b) films on silicon wafers.

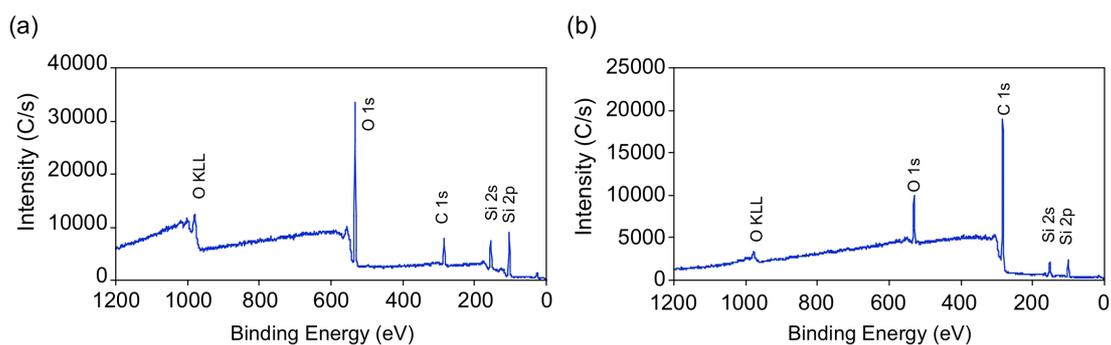


Figure S7. XPS spectra of whole scanning range on the surface of **CuSP1** (a) and **ZnSP1** (b) films.

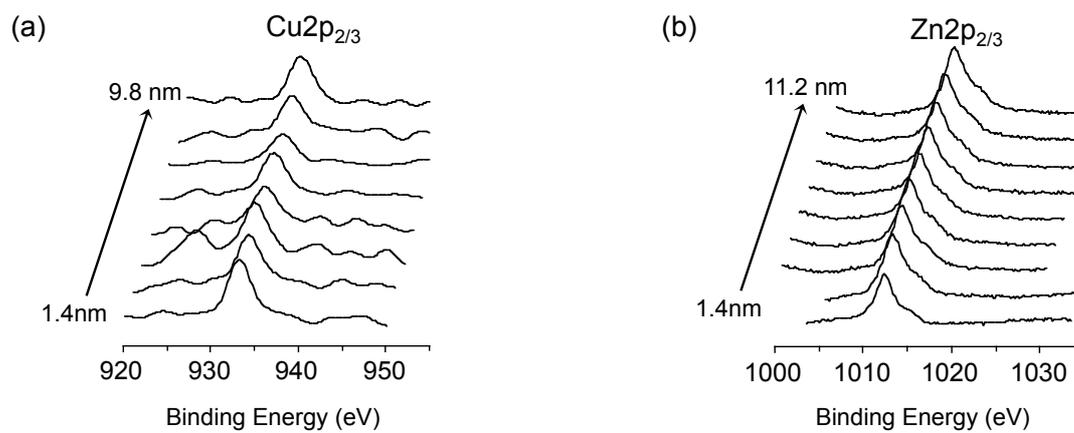


Figure S8. XPS spectra of peaks of Cu_{2p} on **CuSP1** (a) and Zn_{2p} on **ZnSP1** (b) films recorded.

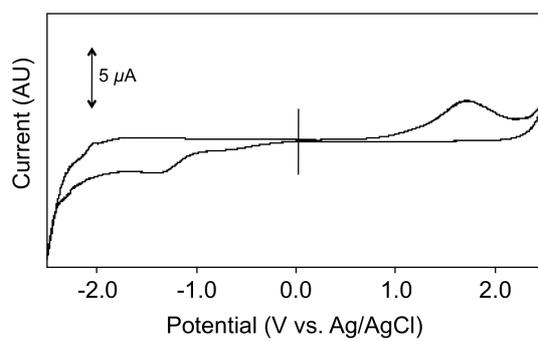


Figure S9. Cyclic voltammetric diagram of **ZnSP2** cast film on an ITO-coated glass substrate.

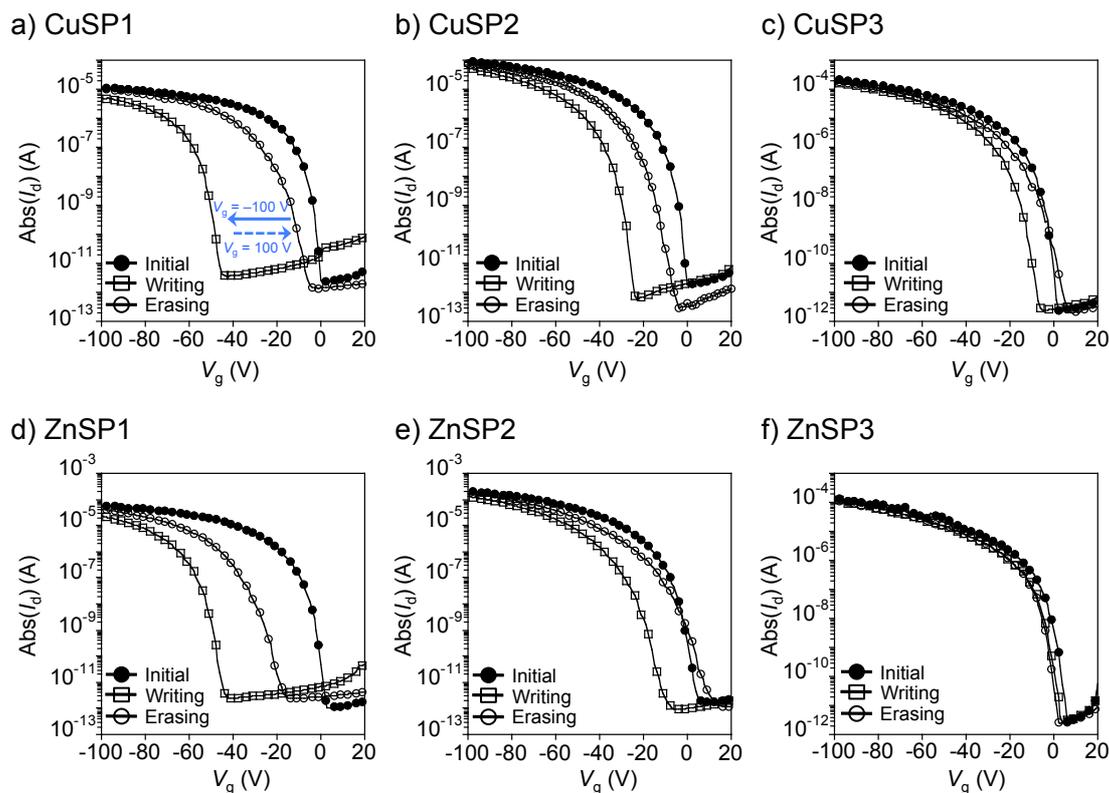


Figure S10. Transfer characteristics of the pentacene OFET memory devices with a) **CuSP1**, b) **CuSP2**, c) **CuSP3**, d) **ZnSP1**, e) **ZnSP2** and f) **ZnSP3** charge storage layers at initial state (black dots), after writing at $V_g = -100$ V for 1s (white square) and after erasing at $V_g = 100$ V for 1s (white circle).

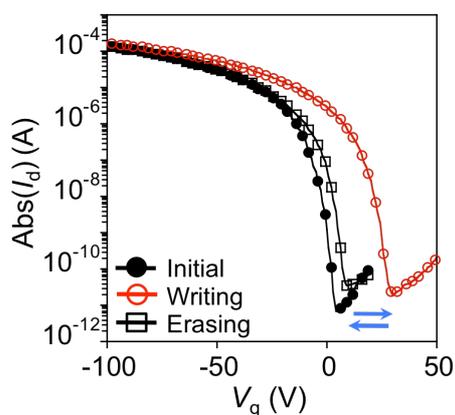


Figure S11. Transfer characteristics of the pentacene OFET memory devices with polystyrene ($M_n = 2,000$ g mol⁻¹) layers at initial state (black dots), after writing at $V_g = 100$ V for 1s (red circle) and after erasing at $V_g = -100$ V for 1s (white square).

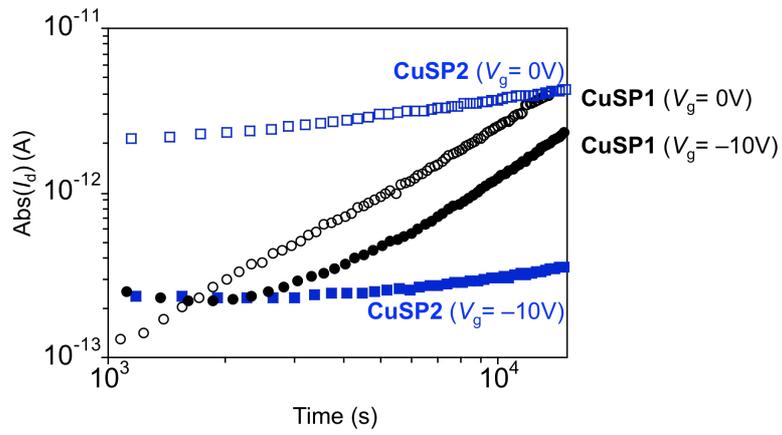


Figure S12. Retention time of I_d of CuSP1 and CuSP2 monitored at $V_g = 0V$ and $-10V$ after writing process ($V_g = -100V$ for 1s).

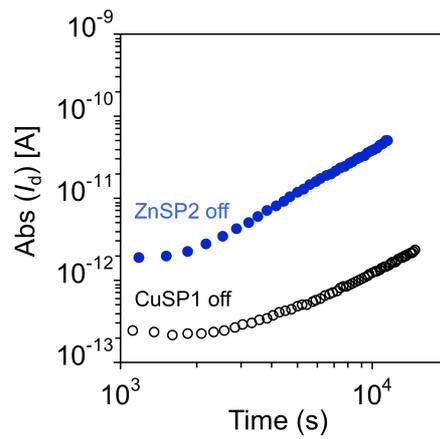


Figure S12. Retention time of CuSP1 (black dots) and ZnSP1 (blue dots) monitored at $V_g = -10V$ after writing (OFF state) at $V_g = -100V$.