

Electronic Supplementary Information (ESI) for

**Recyclable and Photocontrollable Resistive Memory Based on
Polycoumarinsiloxanes**

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Characterization

^1H NMR, ^{13}C NMR and ^{29}Si NMR spectra were measured on a Bruker AV400 (400MHz) spectrometer. Chemical shifts (δ) are given in parts per million (ppm) relative to tetramethylsilane (TMS; $\delta = 0$) as the internal reference. ^1H NMR spectra data are reported as chemical shift, relative integral, multiplicity (s=singlet, d=doublet, m=multiplet), coupling constant (J in Hz) and assignment.

Mass spectrometric measurements were performed on a Agilent-G540 MALDI-TOF mass spectrometer using acetonitrile as the matrix.

Gel permeation chromatography (GPC) analysis was carried out on a Waters 515-2410 system using polystyrene standards as molecular weight references and tetrahydrofuran (THF) as the eluent.

Differential scanning calorimetry (DSC) was performed on a TA Q2000 Differential Scanning Calorimeter at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from 25 to $200\text{ }^\circ\text{C}$ under nitrogen atmosphere. The glass transition temperature (T_g) was determined from the second heating scan.

Thermogravimetric analysis (TGA) was undertaken with a METTLER TOLEDO TGA/DSC 1/1100SF instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of $10\text{ }^\circ\text{C min}^{-1}$ from 25 to $800\text{ }^\circ\text{C}$.

Fourier transform infrared (FTIR) spectra were recorded using a Perkin Elemer SP100 Fourier transform infrared spectrometer in the range of $400 - 4000\text{cm}^{-1}$.

UV-vis absorption spectra were recorded at room temperature from 250 to 600 nm with a Hitachi U-2900 recording spectrophotometer.

Fluorescence spectra were measured on a Shimadzu RF-5301PC Spectrofluorophotometer from 300 to 700 nm.

Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane at room temperature with a CHI 660E voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl pseudo-reference electrode with ferrocenium-ferrocene (Fc^+/Fc) as the internal standard. Cyclic voltammograms were obtained at scan rate of 100 mV s^{-1} . The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram.

The morphologies of polymer films coated on the ITO substrate were measured using

atomic force microscopy (Agilent-5500 AFM) under tapping mode using silicon cantilevers with spring constant of 20-30 N/m. The resonance frequencies were set as 140-160 kHz and the scan speed varied from 0.5-1.0 line/s.

The sandwich structure of the storage cell was measured using scanning electron microscope (JEOL JSM-6300) by scanning the cross section.

The thickness of polymer films is measured by Profiler (BrukerDektak-XT).

The current density-voltage (J-V) characteristics of the sandwich devices were recorded by a Keithley 4200 SCS semiconductor parameter analyzer (Keithley, Cleveland, OH) equipped with a Micromanipulator 6150 probe station in a clean and metallicly shielded box in ambient environment.

Molecular simulations of the basic unit were carried out using the Gaussian 09 software package. The molecular orbital and electronic properties were calculated according to density functional theory (DFT). DFT optimizations using the B3LYP functional with the 6-31G (d) basis set with an RMS force threshold of 1×10^{-4} (tight convergence criteria).

Materials

All reagents were commercially available without any purification except toluene and tetrahydrofuran, they were distilled with sodium and benzophenone before use.

Synthesis

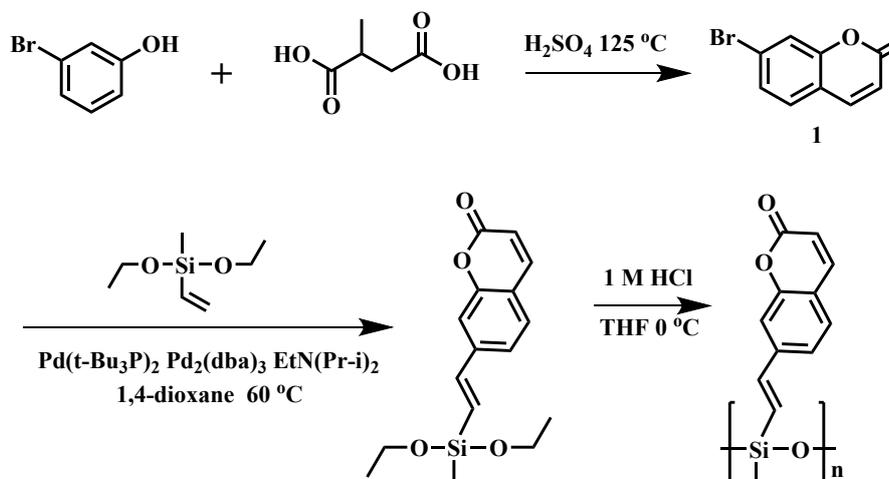
Synthesis of 7-bromocoumarin (1)

10 ml 98% concentrated sulfuric acid were slowly added into 50 ml two-necked round-bottom flask containing m-bromophenol (5 g, 28.9 mmol) and malic acid (2.6 g, 19.4 mmol) at 0 °C under the argon atmosphere. After stirring two hours at room temperature, the reaction were heated to 120 °C gradually and stirred for another 6 h. The mixture was cooled to room temperature naturally and washed with saturated sodium chloride aqueous solutions and extracted with dichloromethane. The organic layer was dried over anhydrous magnesium sulfate. The solvents were distilled under reduced pressure. The crude product was purified by column chromatography (petroleum ether : dichloromethane = 2:1) to get the white solid (yield 60 %). ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 9.6 Hz, 1H), 7.51 (d, *J* = 1.6 Hz, 1H), 7.41 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 6.43 (d, *J* = 9.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 160.01, 154.42 (s), 142.85 (s), 128.91 (s), 128.01 (s), 125.93 (s), 120.34 (s), 117.88 (s), 117.03 (s). MS [M+H]: 223.95; calculated: 224.95.

Synthesis of 7-(diethoxy(methyl)vinyl)-coumarin (2)

In a two-necked round bottom flask, 7-bromocoumarin (900 mg, 4 mmol), EtN(Pr-i)₂ (6 mmol, 780 mg) were dissolved into the solution of Pd(t-Bu₃P)₂ (20 mg, 0.04 mmol) and

$\text{Pd}_2(\text{dba})_3$ (54.9 mg, 0.06 mmol) in 5 ml dry 1,4-dioxane at room temperature under argon atmosphere. Then, methylvinyl-diethoxysilane (960 mg, 6 mmol) was placed in a constant voltage funnel and added to the flask dropwise. Subsequently, the reaction was heated to 60 °C. After being stirred 12 h, the reaction was quenched with water, and extracted with dichloromethane. Then, the organic layer was washed with saturated sodium chloride aqueous solutions and water three times respectively; and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on silica gel (petroleum ether : dichloromethane = 3:1) to yield 510 mg slightly yellow liquid (yield 42%). ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 9.5$ Hz, 1H), 7.44 (d, $J = 8.4$ Hz, 1H), 7.38 (d, $J = 6.6$ Hz, 2H), 7.11 (d, $J = 19.3$ Hz, 1H), 6.47 (s, 1H), 6.45-6.37 (m, 1H), 4.00-3.56 (m, 4H), 1.26 (t, $J = 7.0$ Hz, 6H), 0.29 (d, $J = 8.5$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.63 (s), 154.24 (s), 145.10 (s), 142.79 (s), 141.36 (s), 127.74 (s), 126.81 (s), 122.53 (s), 118.60 (s), 116.32 (s), 114.51 (s), 58.34 (s), 18.20 (s), -4.44 (s). ^{29}Si NMR (79 MHz, CDCl_3) δ -17.91 (s). MS $[\text{M}+\text{H}]$: 304.11; calculated 305.12.



Scheme S1. Synthetic route to PCoumSi.

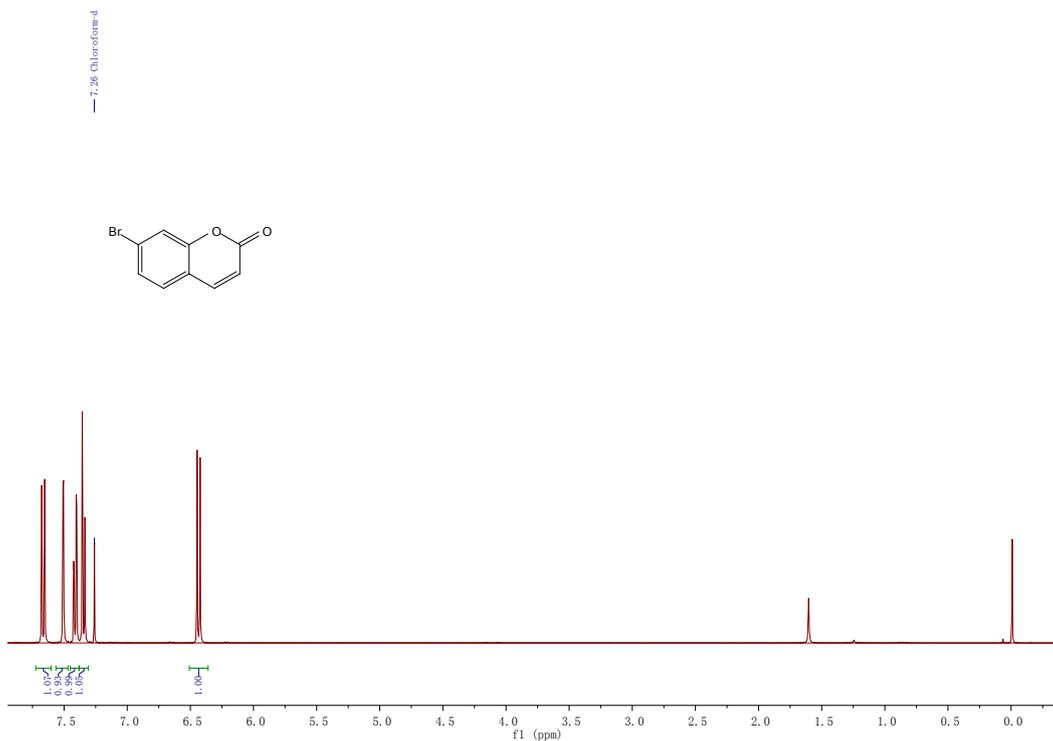


Figure S1. ^1H NMR of 7-bromocoumarin.

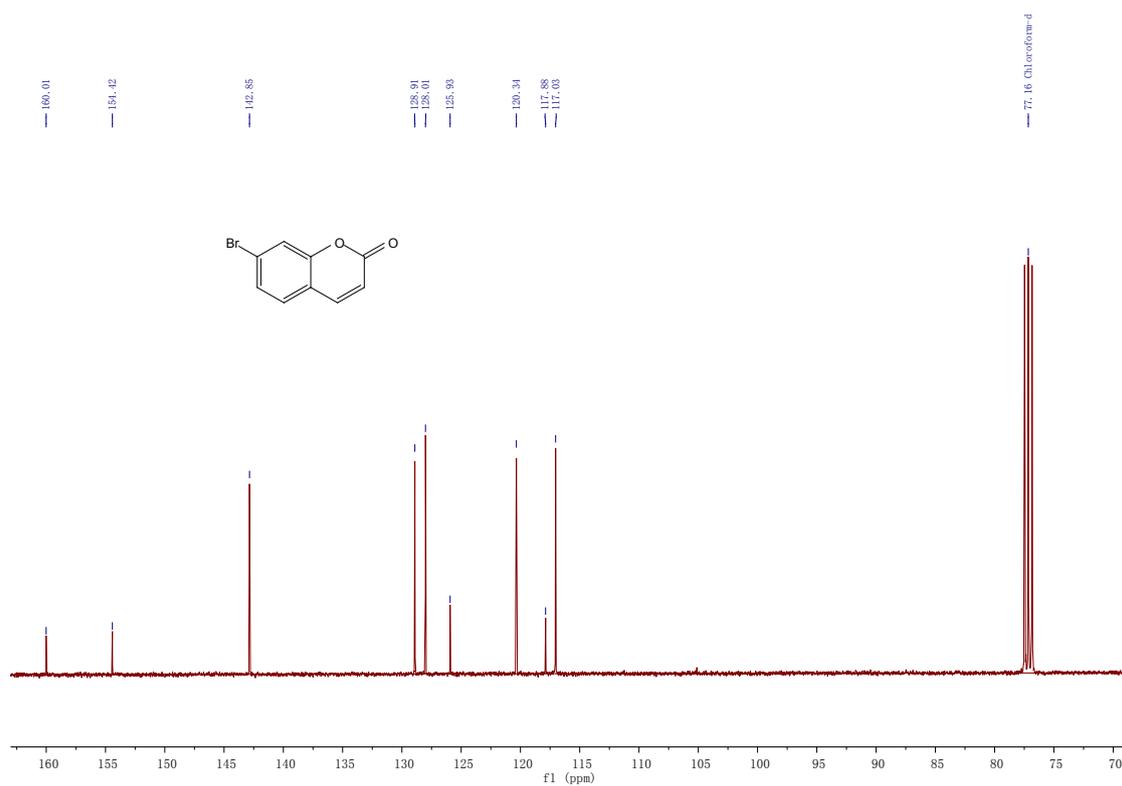


Figure S2. ^{13}C NMR of 7-bromocoumarin.

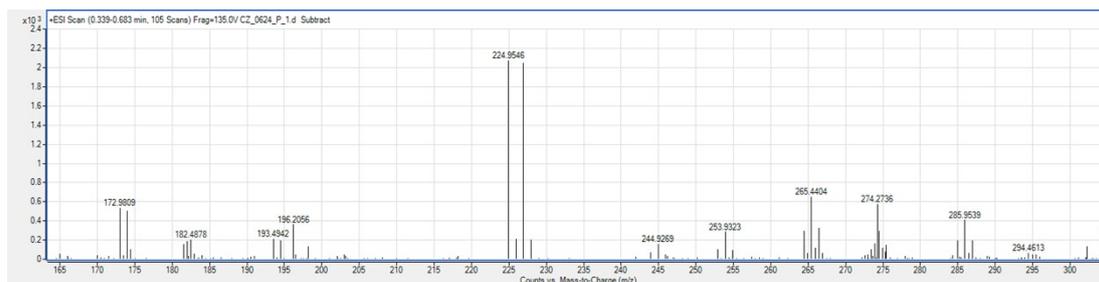


Figure S3. MS spectrum of 7-bromocoumarin.

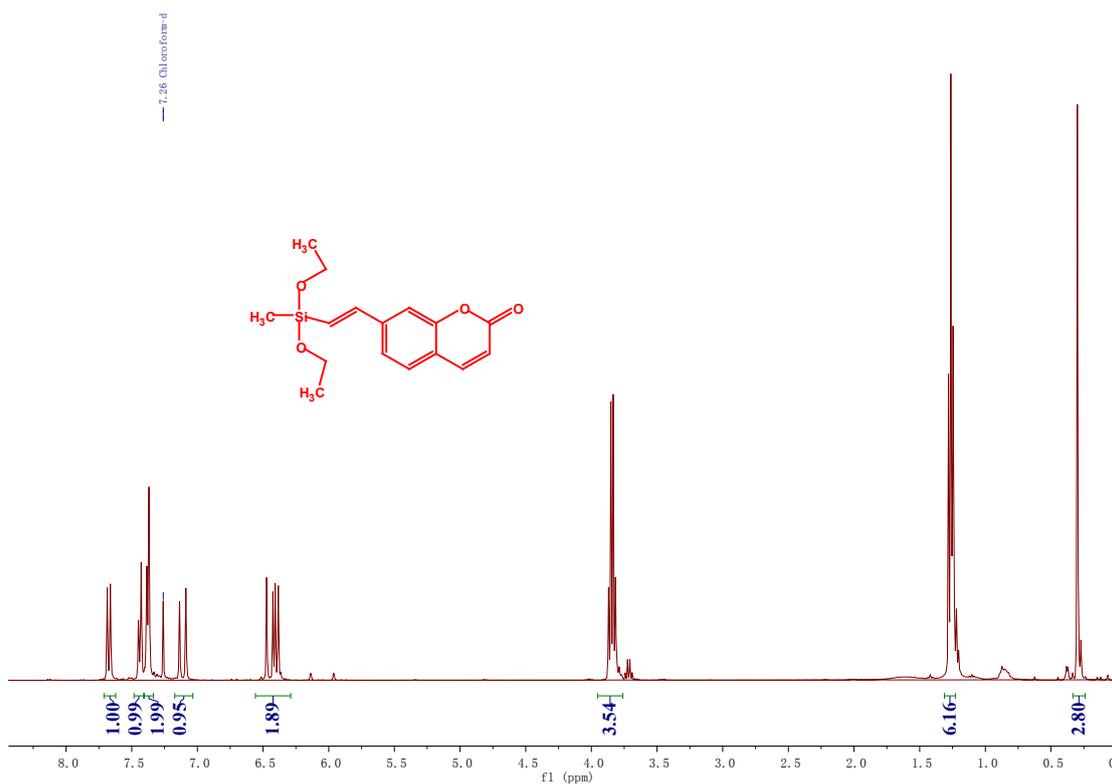


Figure S4. ^1H NMR of 7-(diethoxy(methyl)vinyl)-coumarin.

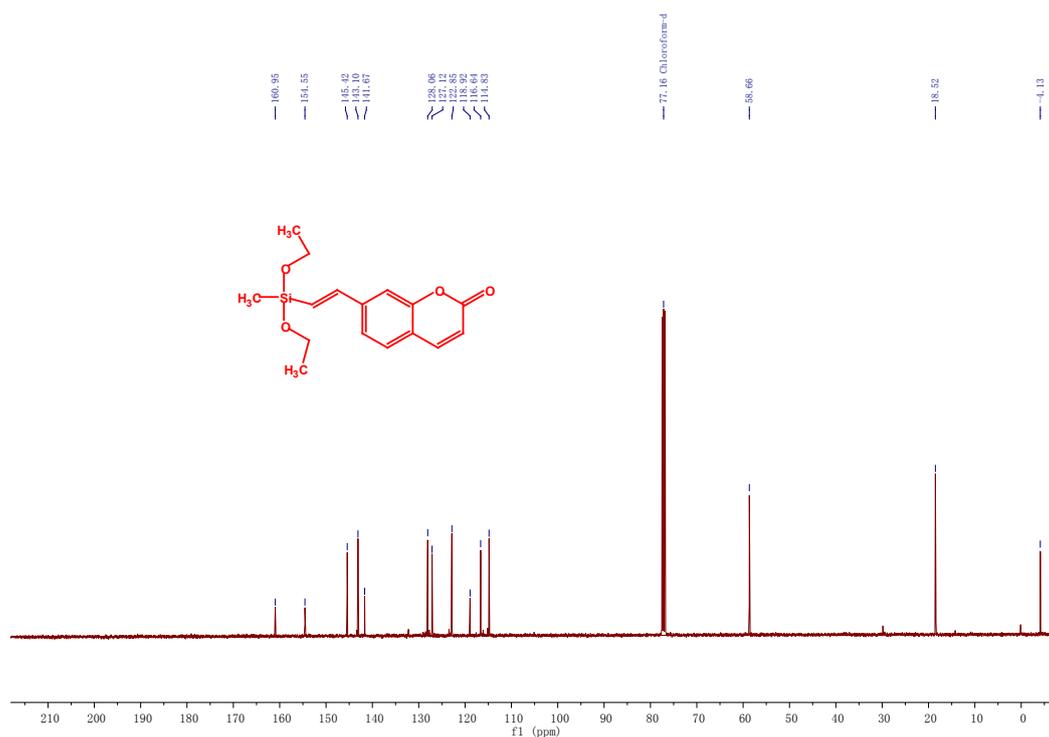


Figure S5. ¹³C NMR of 7-(diethoxy(methyl)vinyl)-coumarin.

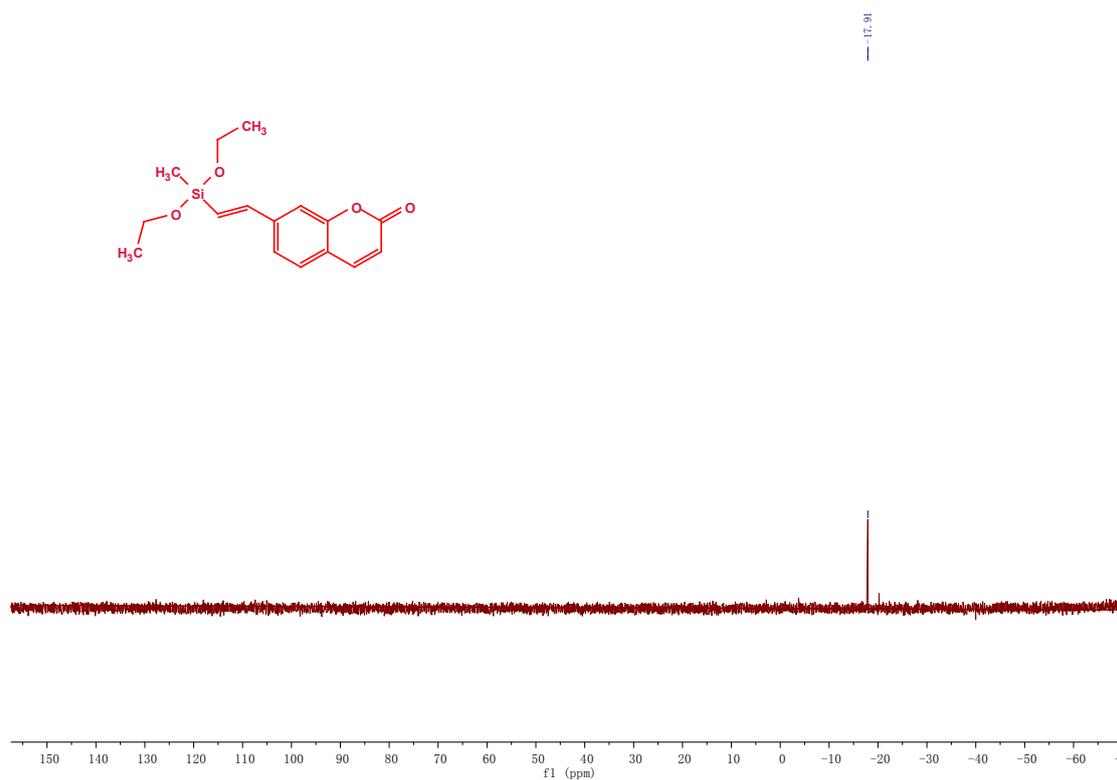


Figure S6. ²⁹Si NMR of 7-(diethoxy(methyl)vinyl)-coumarin.

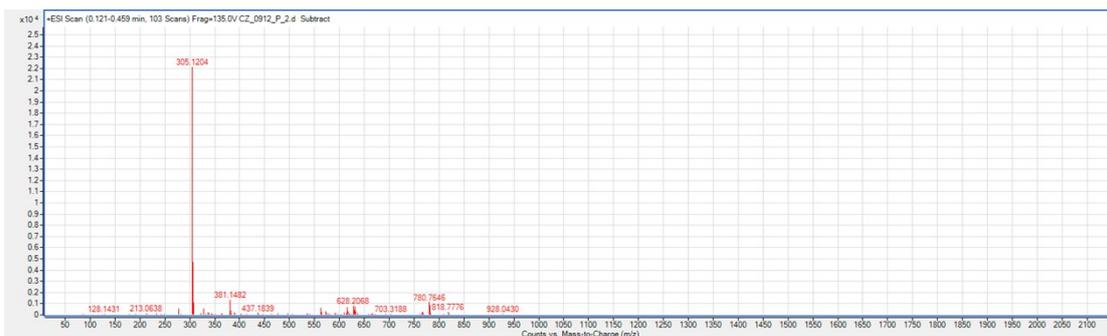


Figure S7. MS spectrum of 7-(diethoxy(methyl)vinyl)-coumarin.

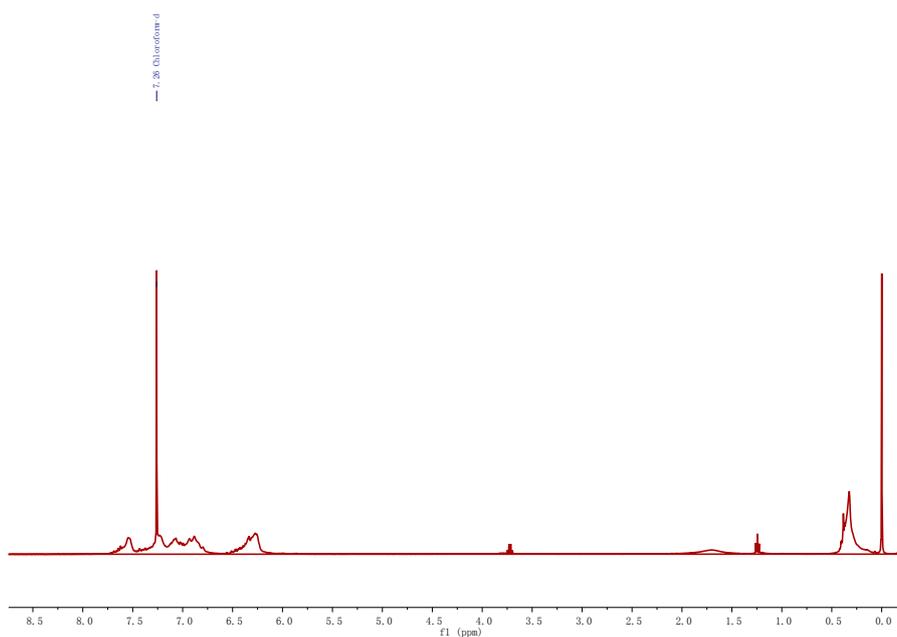


Figure S8. ^1H NMR of PCoumSi.

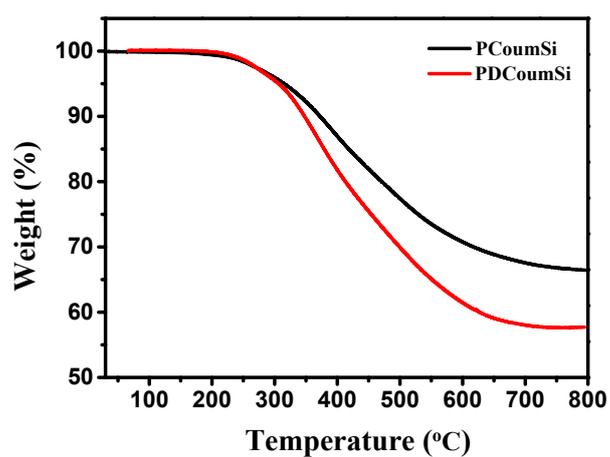


Figure S9. TGA curves of PCoumSi and PDCoumSi.

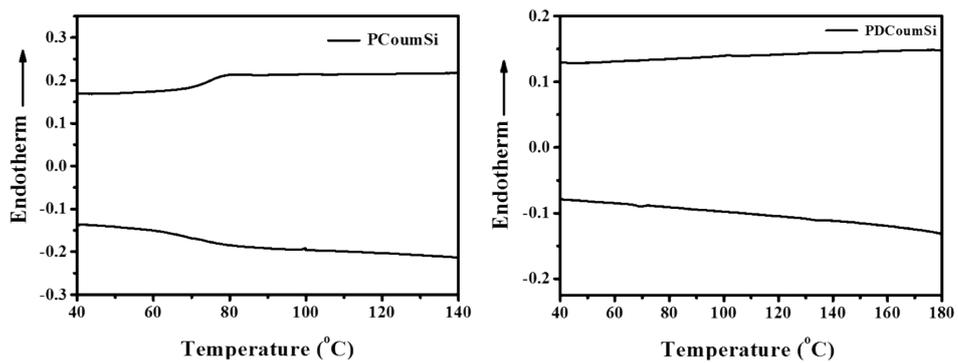


Figure S10. DSC curves of PCoumSi and PDCoumSi.

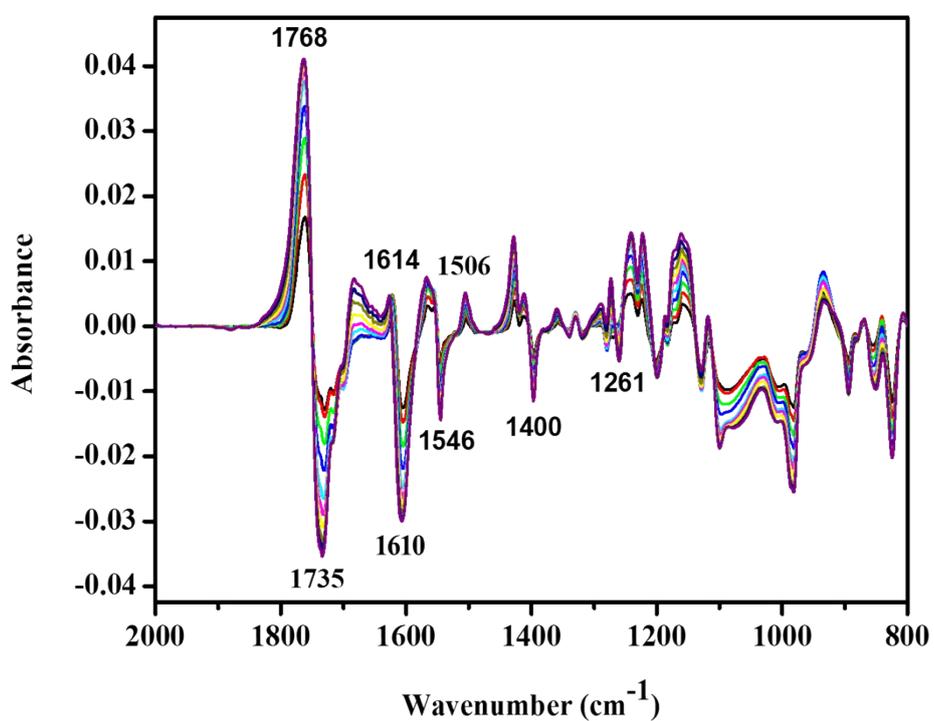


Figure S11. FTIR differential spectra of PCoumSi during photoirradiation by a UV light with the wavelength of 365 nm.

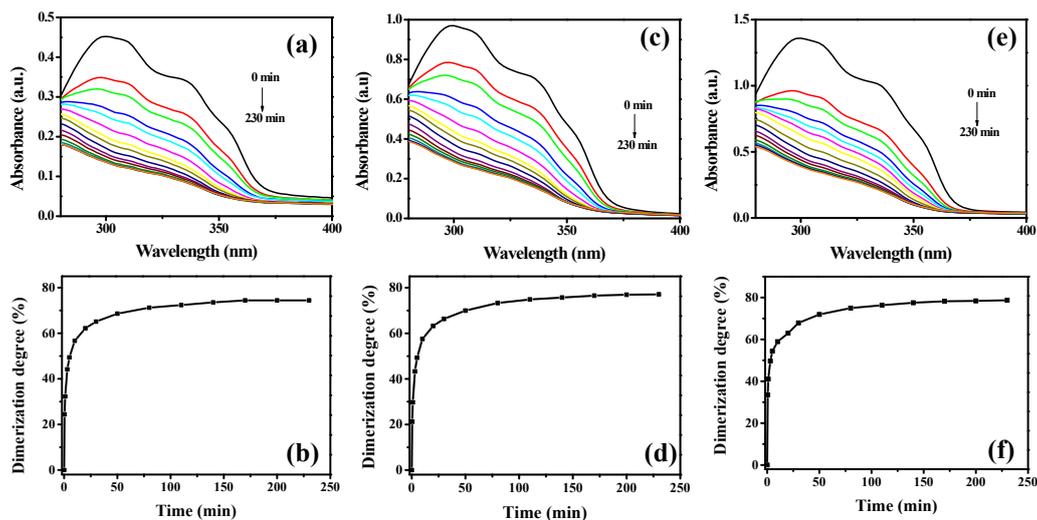


Figure S12. The UV-vis spectral changes of PCoumSi with the different film thicknesses during photoirradiation by a UV light with the wavelength of 365 nm and the calculated corresponding dimerization degree. a&b: 35 nm; c&d: 80 nm; e&f: 130 nm.

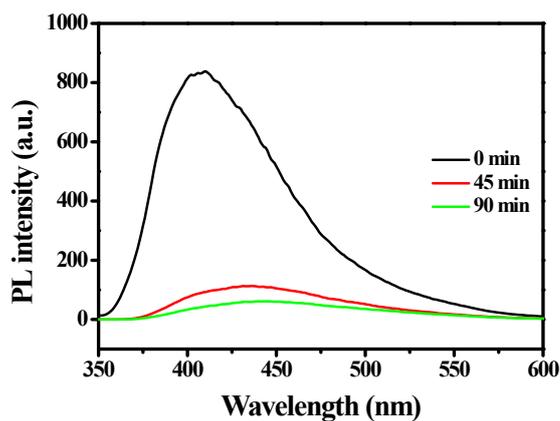


Figure S13. The photoluminescence changes of PCoumSi with the different times during photoirradiation by a UV light with the wavelength of 365 nm.

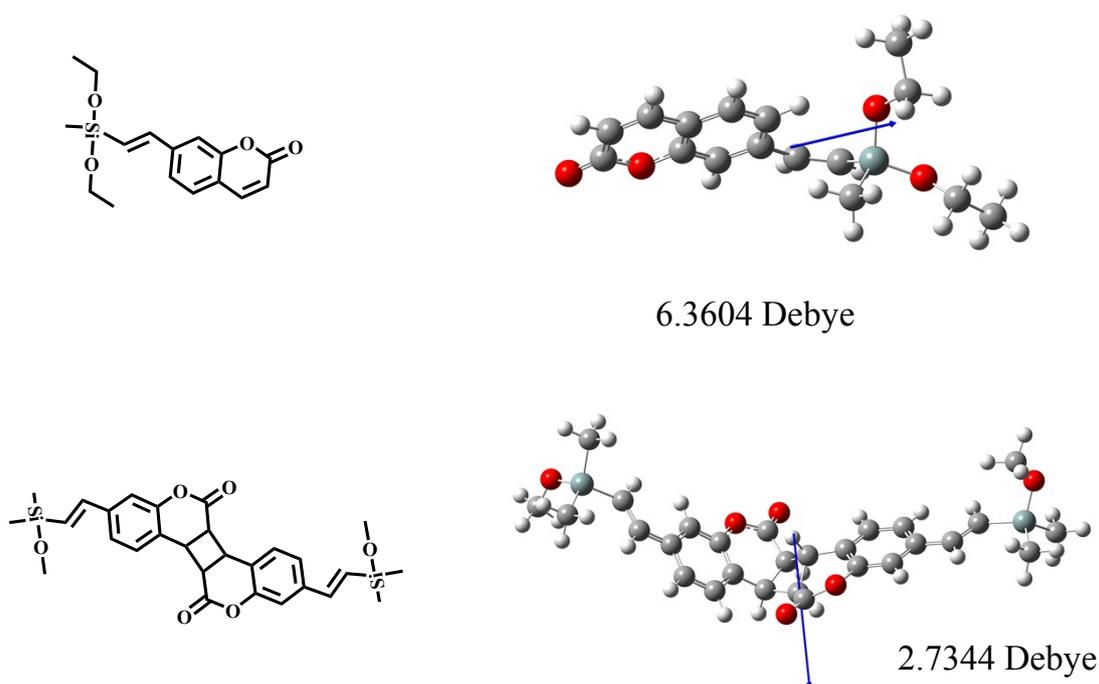


Figure S14. The calculated dipole moments of monomer units of PCoumSi and PDCoumSi.

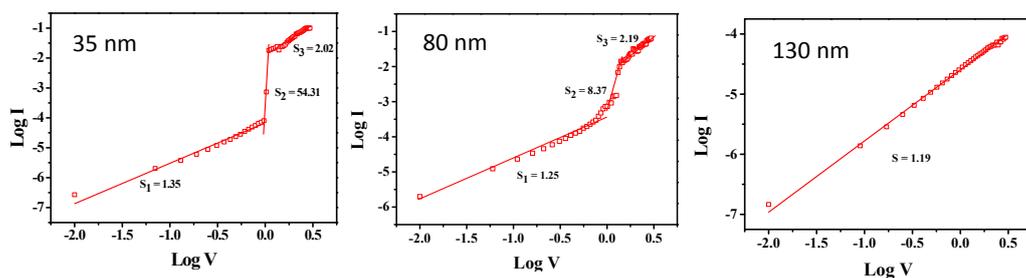


Figure S15. I-V fittings of the first positive sweep for the memory devices with different thickness of the active layer.

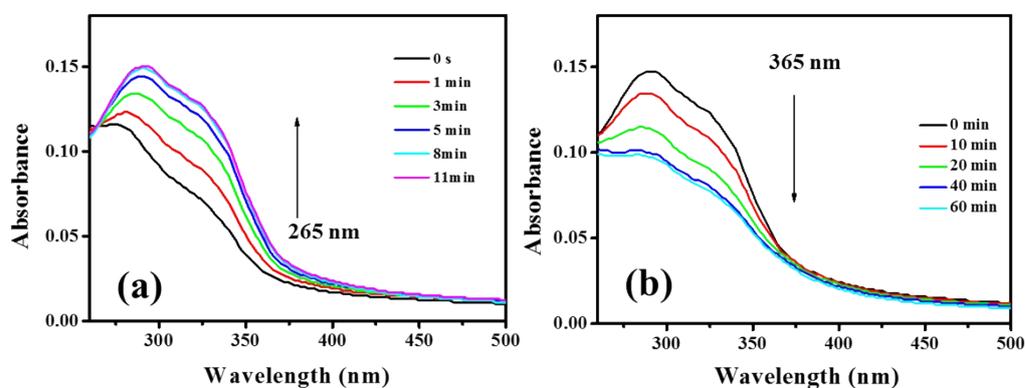


Figure S16. UV-vis spectra of PDCoumSi irradiating with 265 nm light for the different times (a) and then irradiating with 365 nm light again for the different times.

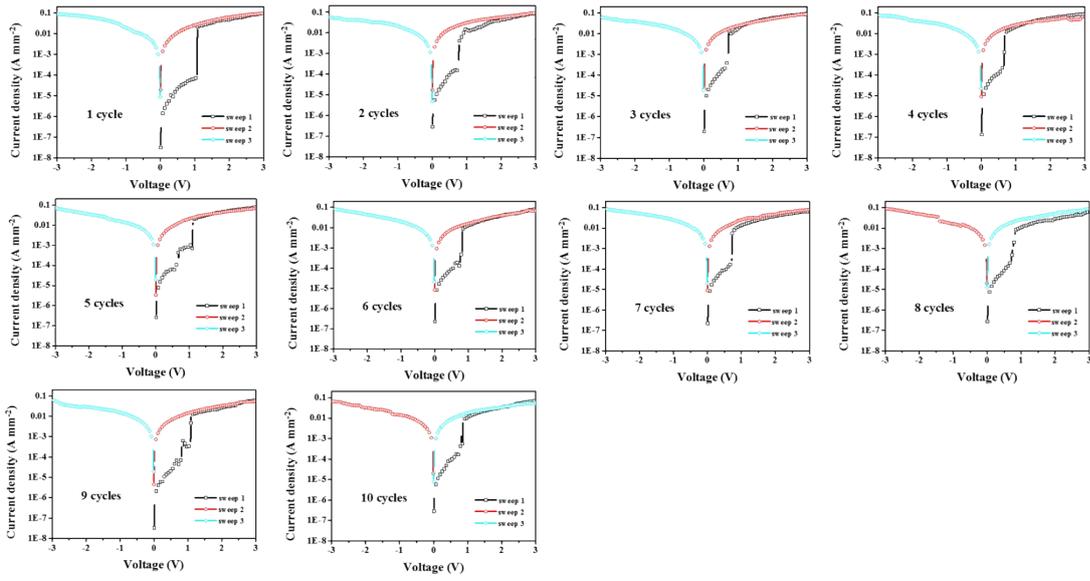


Figure S17. The typical J - V characteristics of the memory device for PDCoumSi with the different cycles.