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Supplementary Information

Controllable Binary/Ternary Memory Behavior Induced by Isomerization of Phenylhydrazone Groups in Polymer Side Chains under Ultraviolet Light Condition

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1. Materials and Methods

Materials

Ethyl 2-(4-hydroxyphenyl)-2-oxoacetate (95%) was purchased from Bidepharm; Phenylhydrazine (98%), methacryloyl chloride (90%) azobisisobutyronitrile (AIBN) (98%) were all purchased from TCI. Acetic acid (AR) and triethylamine (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. AIBN was used after recrystallization with ethanol. All other chemicals were used as received without any further purification.

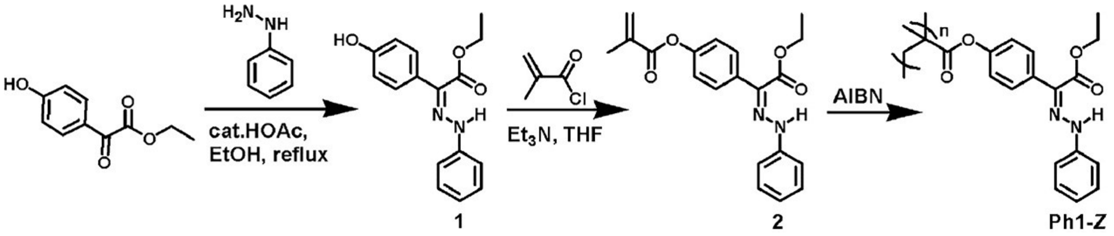
Characterization Methods

The chemical structure was characterized by Nuclear Magnetic Resonance (NMR) on a INOVA 400 MHz FT-NMR spectrometer with the solvent of $CDCl_3$; The number average relative molecular weight and molecular weight distribution of the polymer were measured by gel permeation chromatographs (GPC) on a Waters1515 series using Tetrahydrofuran (THF) as the eluent; Thermogravimetric analysis (TGA) was studied over a PE TGA-7 thermogravimetric analyzer with a flow rate of 10 °C/min; UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer; Cyclic Voltammetry (CV) experiments were conducted by a CorrTest CS Electrochemical workstation analyzer with the scanning speed of 100 mV/s; X-ray diffraction (XRD) was carried out by X-Pert-Pro MPD X-ray diffractometer; Electric storage performance (Current-Voltage curve) was performed on a Keithley 4200-SCS semiconductor characterization system, the memory behaviors were measured at room temperature; Atomic Force Microscope (AFM) images were collected on Bruker Icon AFM platform in tapping model then analyzed and exported by NanoScope Analysis software from the same corporation; XD-300 high brightness cold light source and filters were used as light source.

Fabrication of Memory Device

The substrate of indium tin oxide (ITO) glass was cleared in an ultrasonic bath for 20 min with deionized water, acetone and ethanol, respectively. Ph1-*Z* was dissolved in *o*-dichlorobenzene (10 mg/mL), the solution then was filtered by a microfilter equipped with a 0.22 μm sized pinhole. The organic active layer was obtained through spincoating the polymer solution onto the ITO substrate (a low speed at 500 r/min for 5 seconds followed by high speed at 1200 r/min for 15 seconds). An aluminum (Al) layer was thermally evaporated to the surface of organic layer as the top electrode under high vacuum of 10^{-5} Torr through a metal mask to obtain the final sandwich-type memory device.

2. Synthesis details



Scheme S1. Synthesis of Ph1-*Z* polymer.

Synthesis of ethyl (*Z*)-2-(4-hydroxyphenyl)-2-(2-phenylhydrazono)acetate (Compound 1)

Ethyl 2-(4-hydroxyphenyl)-2-oxoacetate (2.10 g, 10.80 mmol) and 150 mL EtOH were mixed in a 250 mL flask, following by adding phenylhydrazine (1.20 mL, 12.00 mmol) and a few drops of acetic acid. Then the mixture was refluxed for 3 h under N_2 condition, cooled to room temperature after the reaction was completed, then extracted with ethyl acetate, the organic phrase was washed with saturated NaCl solution, dried with anhydrous Na_2SO_4 and concentrated under reduced pressure to obtain the crude product, which was further purified by silica gel column chromatography (eluent: ethyl acetate/petroleum ester=1/10, v/v) to give a yellow solid (2.45 g, 80 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.32 (s, 1H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 4.0 Hz, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.88 – 6.81 (m, 2H), 5.00 (s, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H).

[1]Synthesis of (*Z*)-4-(2-ethoxy-2-oxo-1-(2-phenylhydrazono)ethyl)phenyl methacrylate (Compound 2)

Compound 1 (2.28 g, 8.00 mmol), triethylamine (1.70 mL) and 25 mL THF were added in a 50 mL round-bottom flask at 0 °C. Then a mixture of methacryloyl chloride (1.25 g, 12.00 mmol) and THF (5 mL) was slowly added to the reaction. After stirring in an ice bath for 10 h, the mixture was extracted with dichloromethane, then dried with anhydrous Na_2SO_4 and concentrated under reduced pressure to obtain the crude yellow product, which was further purified by silica gel column chromatography (eluent: dichloromethane/petroleum ester=1/5, v/v) to give a yellow solid (2.11 g, 75 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.45 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.28 (s, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.01 (t, *J* = 7.1 Hz, 1H), 6.37 (s, 1H), 5.77 (s, 1H), 4.36 (p, *J* = 6.8 Hz, 2H), 2.08 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.84, 163.63, 150.35, 143.16, 135.92, 134.15, 129.69, 129.37, 127.30, 122.58, 120.96, 114.28, 61.12, 18.44, 14.21. Elemental analysis (%) calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95; found: C, 67.91; H, 5.64; N, 7.66. MALDI-TOF-MS m/z: calcd 352.14, found 351.85.

Synthesis of the polymer Ph1-*Z*

Compound 2 (264 mg, 0.75 mmol), AIBN (5 mg, 0.03 mmol) and cyclohexanone (5 mL) were mixed in a tube under N_2 condition, the mixture was reacted for 24 h at 75 °C. After the reaction was completed, the obtained reaction liquid was poured into a large amount of methanol to precipitate out the crude product, which was filtered and further purified with methanol in the Soxhlet extraction device to remove small molecules. The yellow solid was obtained after dried (164 mg, 62%).

3. Figures

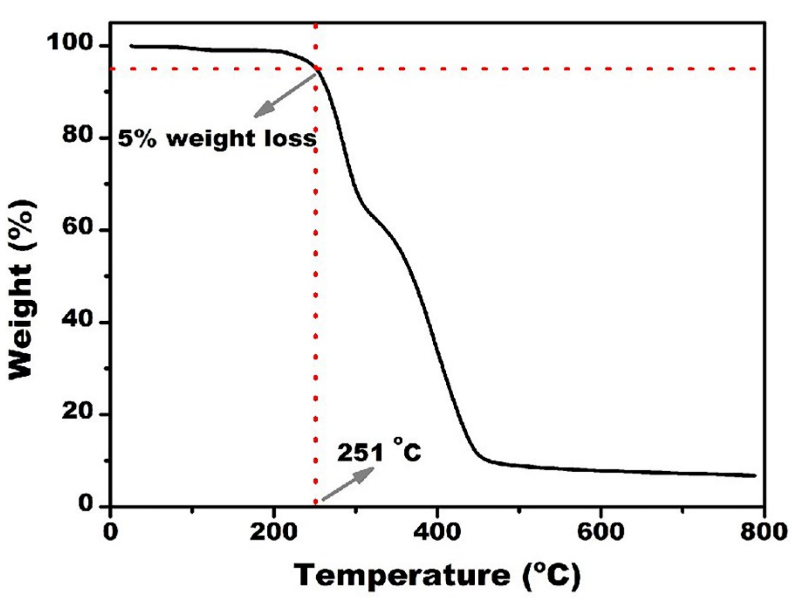


Figure S1. Thermogravimetric curve of Ph1-*Z* in N_2 condition at temperature rising rate of 10 °C/min.

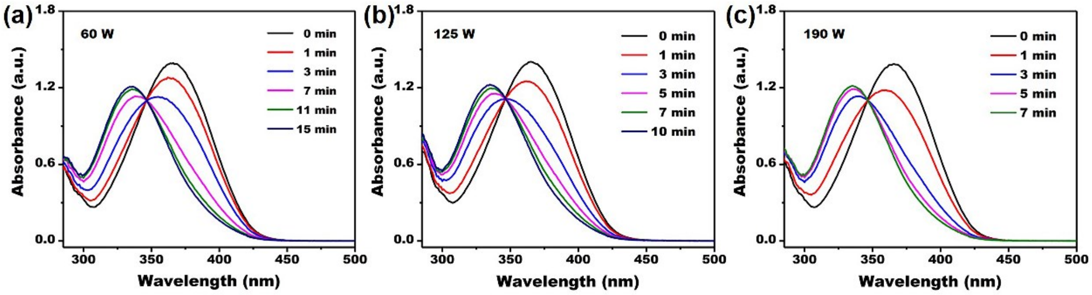


Figure S2. UV-vis absorption spectra of Ph1-*Z* in toluene solution (1×10^{-5} M) under the photoirradiation at 394 nm with different light power: (a) 60 W; (b) 125 W; (c) 190 W. The results show that the light power could efficiently affect the isomerization rate. Considering the principle of energy saving and isomerization efficiency, we choose the middle 125 W as the power for photoirradiation.

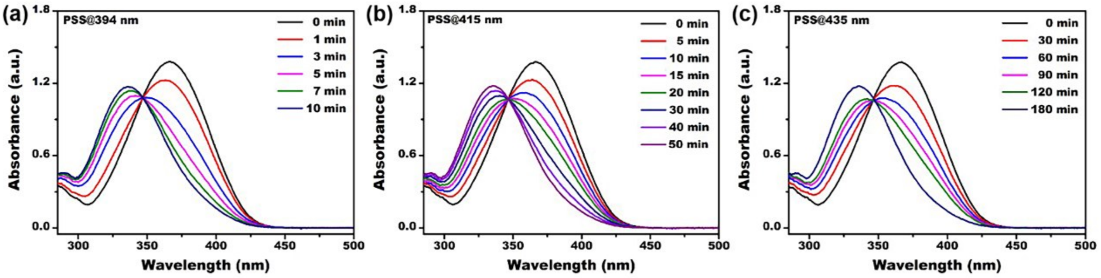


Figure S3. The UV-vis absorption spectra of Ph1-*Z* in toluene solution (1×10^{-5} M) under the photoirradiation at (a) 394 nm, (b) 415 nm and (c) 435 nm, respectively.

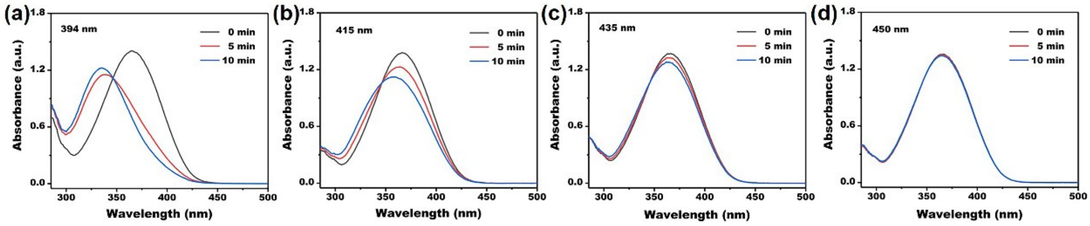


Figure S4. UV-vis absorption spectra of Ph1-*Z* in toluene solution (1×10^{-5} M) under the photoirradiation for 10 min at different wavelengths: (a) 394 nm; (b) 415 nm; (c) 435 nm; (d) 450 nm.

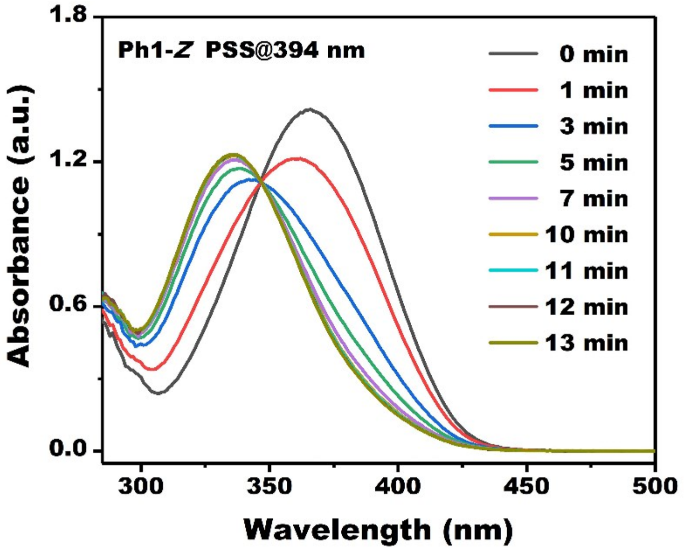


Figure S5. UV-vis absorption spectra of Ph1-Z in toluene (1×10^{-5} M) under continuous photoirradiation at 394 nm for 13 min.

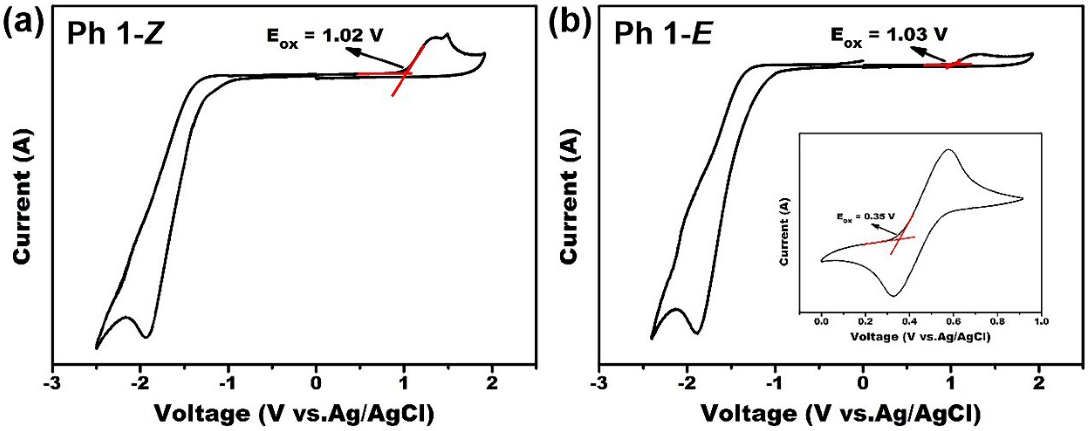


Figure S6. Cyclic voltammetry curves of (a) Ph1-*Z* and (b) Ph1-*E* in the film with a scanning rate of 100 mV/s in acetonitrile (0.1 M $TBAPF_6$).

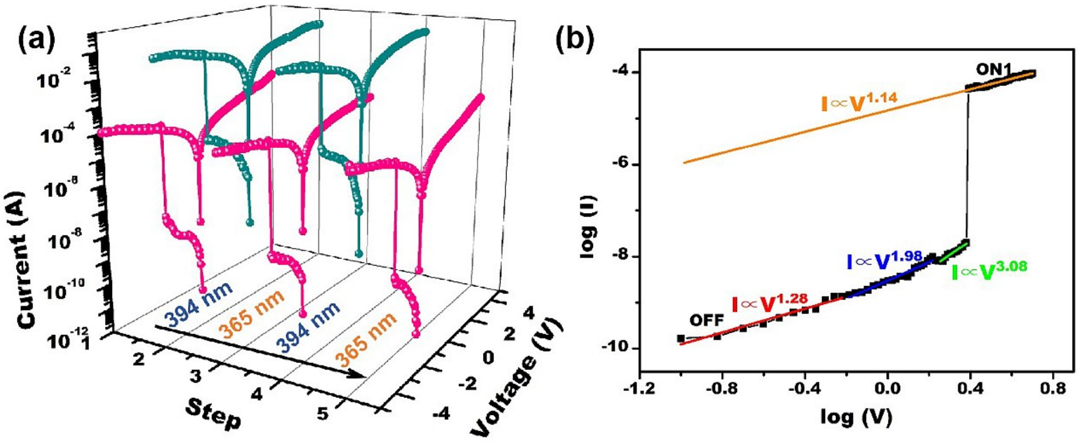


Figure S7. (a) I-V characteristics of the Ph1-*Z*/Ph1-*E* based memory device under the photoirradiation at 394 nm and 365 nm. (b) Double logarithmic curve of the I-V curve on OFF state and ON1 state.

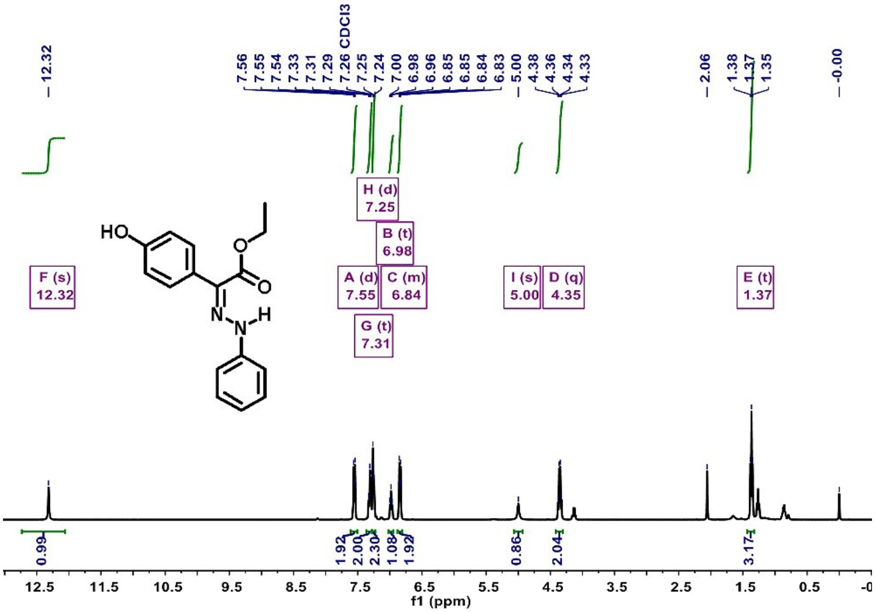


Figure S8. ^{1}H NMR spectrum of compound 1 in $CDCl_3$ with TMS as internal standard.

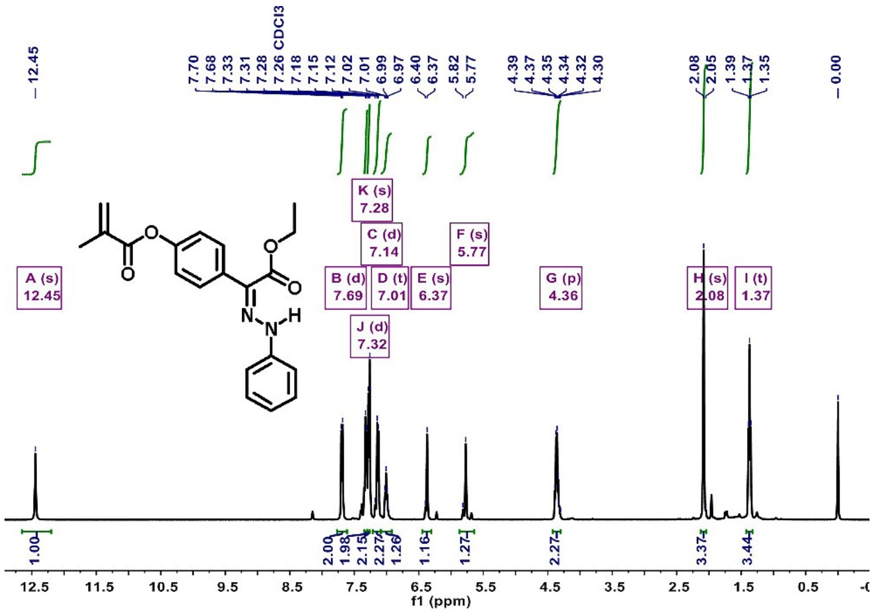


Figure S9. ^{1}H NMR spectrum of h1-*Z* in $CDCl_3$ with TMS as internal standard.

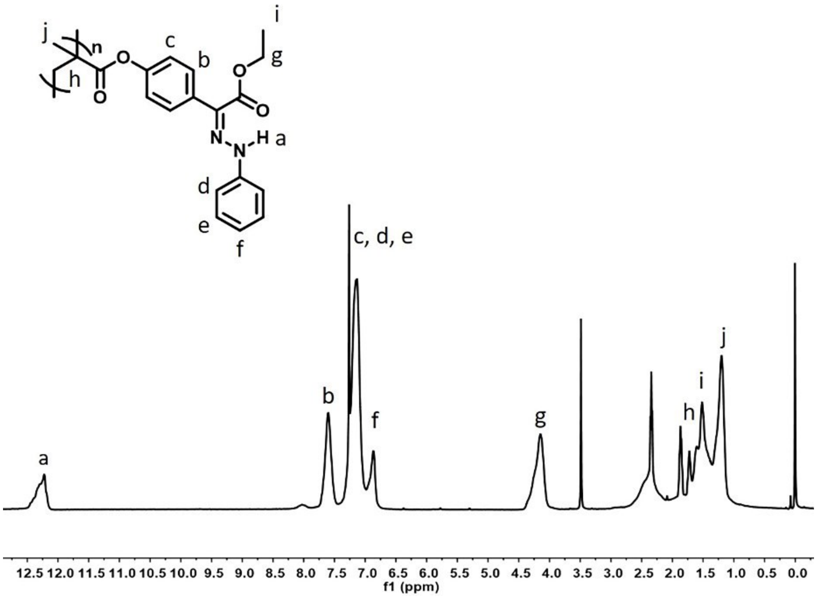


Figure S10. ^{1}H NMR spectra of Ph1-*Z* in the solvent of $CDCl_3$ with TMS as internal standard.

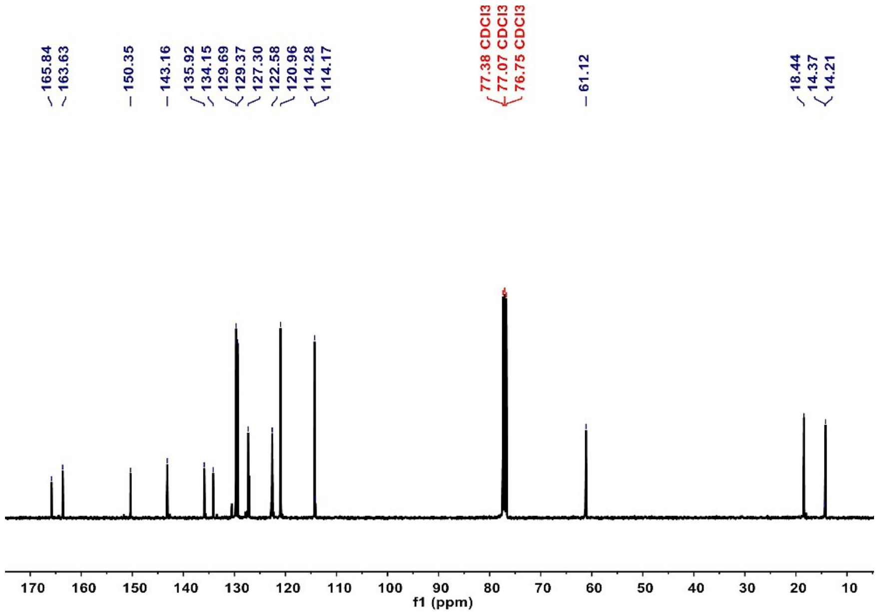


Figure S11. ^{13}C NMR spectrum of h1-*Z* in CDCl$_3$ with TMS as internal standard.

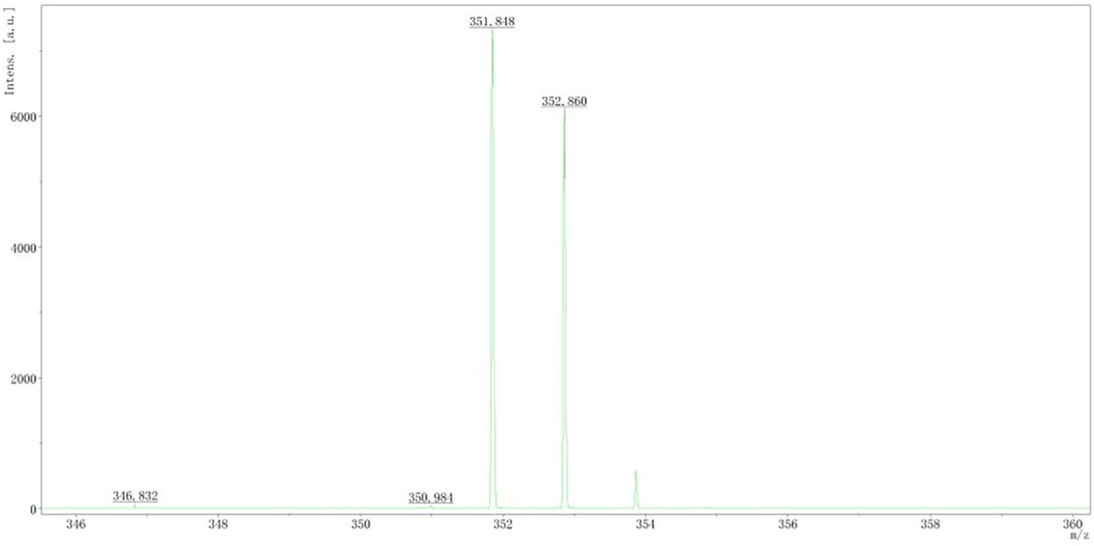


Figure S12. MALDI-TOF mass spectra of h1-*Z*.

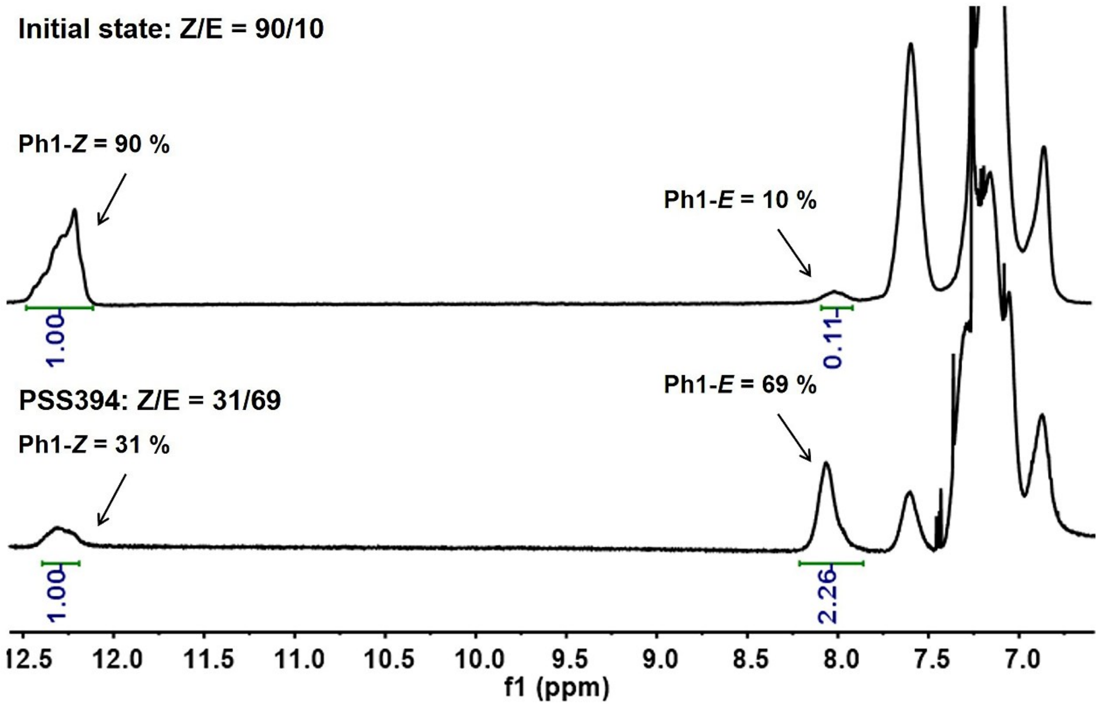


Figure S13. ^{1}H NMR spectra of phenylhydrazone switch Ph1-*Z* before and after photoirradiation at 394 nm to reach PSS in $CDCl_3$.

4. Photoisomerization Quantum Yields

Quantum yield were also calculated as reported as shown below:[2, 3]

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$

In general, the kinetics of a basic photochemical reaction that sample A undergo photoisomerization to generate sample B can be expressed using Eq. 1.

$$r_{A\to B} = \frac{I_0\Phi_{A\to B}}{V}(1–10^{-\varepsilon_A c_A l}) \quad \text{Eq. 1}$$

When the absorbance is less than 0.43, Taylor expansion and truncation at the first−order term can simplify Eq. 1 to Eq. 2, an expression relating the quantum yield, an observed first−order rate constant, molar photon flux, and measurable properties of sample A.

$$k_{A\to B} = \frac{I_0\Phi_{A\to B}}{V}\varepsilon_A \cdot l \cdot ln10 \quad \text{Eq. 2}$$

Eq. 2 can be rearranged into Eq. 3 to calculate the quantum yield $\Phi_{A\to B}$.

$$\Phi_{A\to B} = \frac{k_{A\to B}V}{I_0\varepsilon_A l\ln 10} \quad \text{Eq. 3}$$

Where $\Phi_{A\to B}$ = quantum yield; $k_{A\to B}$ = rate constant (obtained from the exponential fit of a graph of Abs vs. time); V = sample volume; I_0 = molar photon flux; ε_A = molar absorption coefficient; l = light path length.

The molar photon flux I_0 at 394 nm was measured using chemical actinometry.[2, 4] a 2.0 mL aliquot of a 20 mM potassium ferrioxalate solution was placed in an 1.0 cm quartz cuvette and irradiated at 394 nm for 10 min (t_0). The Fe(III) oxalate was reducted to Fe(II) oxalate in this process. The solution was combined with ferrozine (3 equivs). A reddish-purple solution containing $[\mathrm{Fe(ferrozine)_3}]^{2+}$ complex was formed, then diluted by a factor of 30 (n), its absorbance was measured at 563nm with the molar absorption coefficient (ε_{563}) of 27,900 $\mathrm{cm^{-1}\ M^{-1}}$. The molar photo flux I_0 of light source at 394 nm was determined using Eq. 4.

$$I_0(mol\cdot s^{-1}) = \frac{A_{563}\cdot n\cdot V_0}{\varepsilon_{563}\cdot l\cdot t_0\cdot \Phi_{394}} \quad \text{Eq. 4}$$

where l = the length of cuvette; and Φ_{394} indicates the quantum yield of the photo-reduction of Fe(III) oxalate induced by the light source. (Φ_{394}= 1.17)[5]

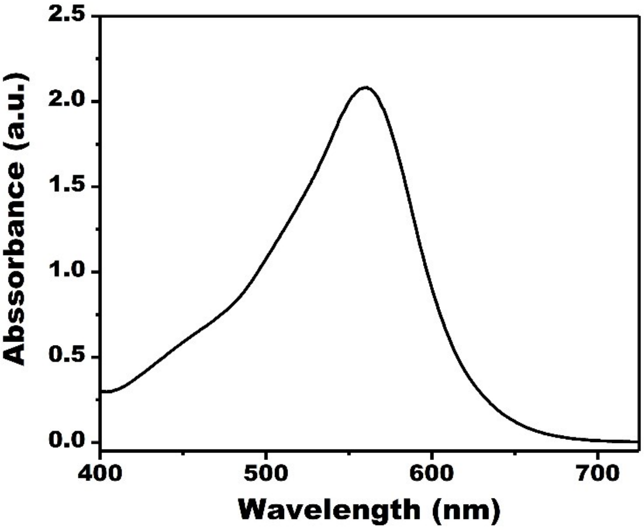


Figure S14. UV-vis absorption spectra of $[\mathrm{Fe(ferrozine)_3}]^{2+}$ after dilution. The absorbance at 563 nm (A_{563}) was determined to be 2.073.

The rate law for the formation of sample B is shown as following Eq. 5

$$C_B = \frac{k_f}{k_f + k_r}C_{total}(1-e^{-(k_f + k_r)t}) \quad \text{Eq. 5}$$

where $C_{total} = C_A + C_B$ represents the total concentration of the photoswitch. k_f and k_r represent the first order approximate rate constants of the forward and reverse photochemical reactions under the low absorption approximation.

The consumption of sample A can be calculated by rearranging Eq. 5 into Eq. 6

$$C_A = \frac{C_{total}\cdot k_r}{k_f + k_r} + \frac{C_{total}\cdot k_f}{k_f + k_r} e^{-(k_f + k_r)t} \qquad \text{Eq. 6}$$

C_A is proportional to the absorbance of sample A. The observed rate constant $k_{obs} = k_f + k_r$ can be obtained from the exponential fit of a graph of Abs vs. time. With the thermal relaxation not be taken into account, $k_{A\to B} \approx k_{obs}$.

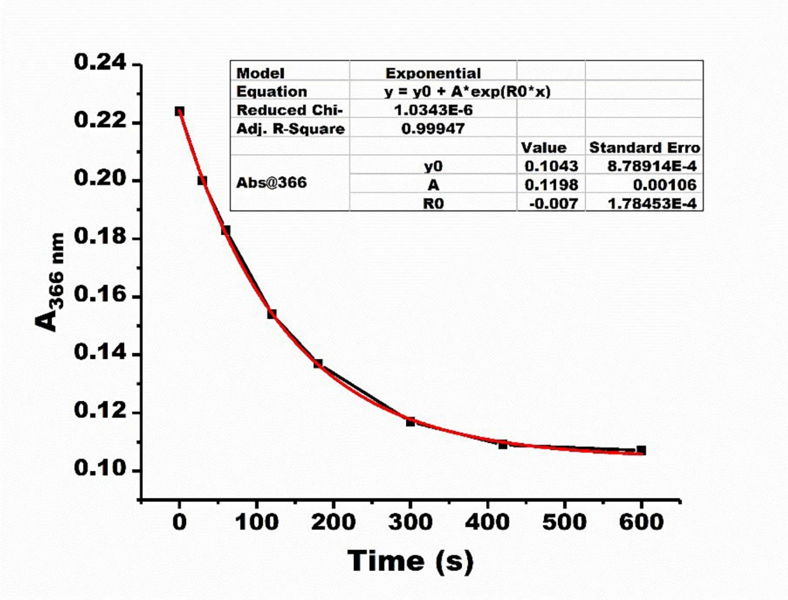


Figure S15. Kinetics for the photoisomerization (irradiation at 394 nm) of Ph1-*Z* to Ph1-*E* in toluene (1.5×10^{-6} M). The plot is of the absorbance at 366 nm of Ph1-*Z* at a function of time. ε_{Ph1-Z} = 149333 $M^{-1}\cdot cm^{-1}$ was used for the quantum yield calculation. The quantum yield was calculated to be 10.3 ± 0.7% based on three consecutive measurements.

5. References

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