Supporting Information

High-performance visible laser rewritable black paper

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1. Experimental section

1.1. Materials and reagents

Resorcine (99 %), 2-(4-diethylamino-2-hydroxybenzoyl) benzoic acid (98 %), trifluoroacetic acid (TFA, 99 %), methanesulfonic acid (CH_3SO_3H, 99 %), phenylhydrazine (98 %), 3-Methyl-2-butanone (98 %), 1,3-Propanesultone (98 %) and salicylaldehyde (98 %) were purchased from Energy Chemical (Shanghai, China). Acidochromic dyes and pH-sensitive dye: 2-Anilino-6-dibutylamino-3-methylfluoran (ODB-2) and 3-diethylamino-7-(2'-chlorophenylamino) fluorane (FH 101) were purchased from Deba Chemical (Shanghai, China). Methyl orange (MO) was purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). Anhydrous sodium sulfade (Na_2SO_4), sodium bicarbonate ($NaHCO_3$) and hydrochloric acid (HCl) were purchased from Beijing Chemical Works (Beijing, China). Solvents: methanol (MeOH, HPLC) was purchased from Yuwang Group (Shandong, China). Ethyl acetate (EtOAc), ethanol (EtOH), dimethyl sulfoxide (DMSO) and dichloromethane (CH_2Cl_2) were purchased from Beijing Chemical. Wahaha purified H_2O (Hangzhou, China) was used for all experiments. PEG 20000 (molecular weight: 17,000–22,000) was purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). Cellulose filter paper (Whatman–Xinhua, grade 91, Hangzhou, China) was selected as the paper substrate.

1.2. Instruments and characterizations

Absorption spectra were measured using Analitik Jena Specord®210 plus UV/VIS spectrophotometer. Reflective spectra were tested via integrating sphere on Analitik Jena Specord®210 plus UV-VIS spectrophotometer, using barium sulfate ($BaSO_4$) as background, slit was 2 cm. CIE L*, a*, b* was measured by X-rite spectrodensitometer. ^1H NMR (400, 500 MHz) spectra was recorded on a Bruker AVANCE400 at room temperature. Blue light source for imaging with a mask here used was Wota F25 fishing lamp (Ningbo, China). Laser automatic printing was realized by laser marking machine Xiai XYC-UV / MGL, which was purchased from Changchun New Industries Optoelectronics Tech. Co. (Changchun, China). Photographs were captured using the Nikon D7100 camera.

1.3. Preparation of black VLRP

The preparation process of black **VLRP** referred to our previous work[S1]. Filter paper was firstly coated with a layer of 10 wt% PEG20000 aqueous solution and then dried by heating at 80 ^oC. Later, it was soaked into a MeOH solution of the acidochromic dyes (5 mM ODB-2 & 0.7 mM Rhodol), P-1 (11.4 mM) and 15 wt% PEG20000 mixture.

2. Synthesis Methods

2.1. Synthesis of P-1

Compound P-1 was reported previously[S1,S2]. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.03 (s, 1H), 8.60 (d, *J* = 16.3 Hz, 1H), 8.28 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.94-7.81 (m, 2H), 7.62 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 4.81 (t, *J* = 7.3, 2H), 2.64 (t, *J* = 6.0 Hz, 2H), 2.18 (m, 2H), 1.77 (s, 6H).

2.2. Synthesis of Rhodol

The synthesis of Rhodol was according to the literature[S3]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.08 (s, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.78 (t, *J* = 7.4 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 6.66 (s, 1H), 6.52 (s, 2H), 6.46 (s, 1H), 6.44 (s, 2H), 3.37-3.32 (m, 4H), 1.09 (t, *J* = 6.9 Hz, 6H).

3. Supplementary Figures

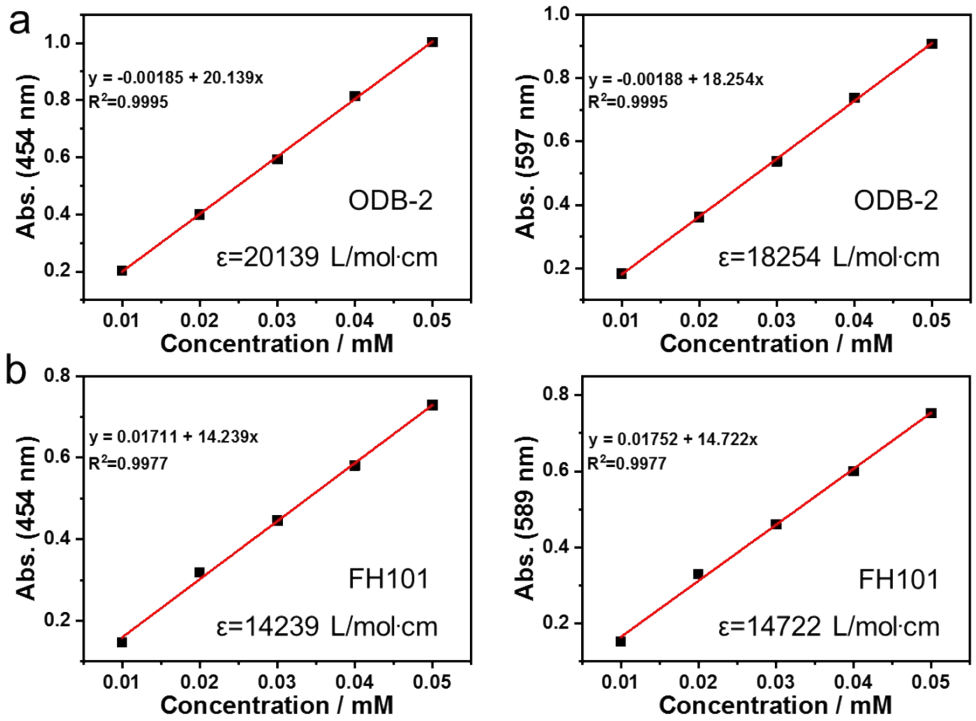

Fig. S1 Plots of the absorbance at two complementary absorption peaks of (a) ODB-2 and (b) FH101 after adding excessive CH_3SO_3H versus increasing concentration and thus its molar absorption coefficients (ε) at two complementary absorption peaks were obtained respectively according to LambertBeer law.

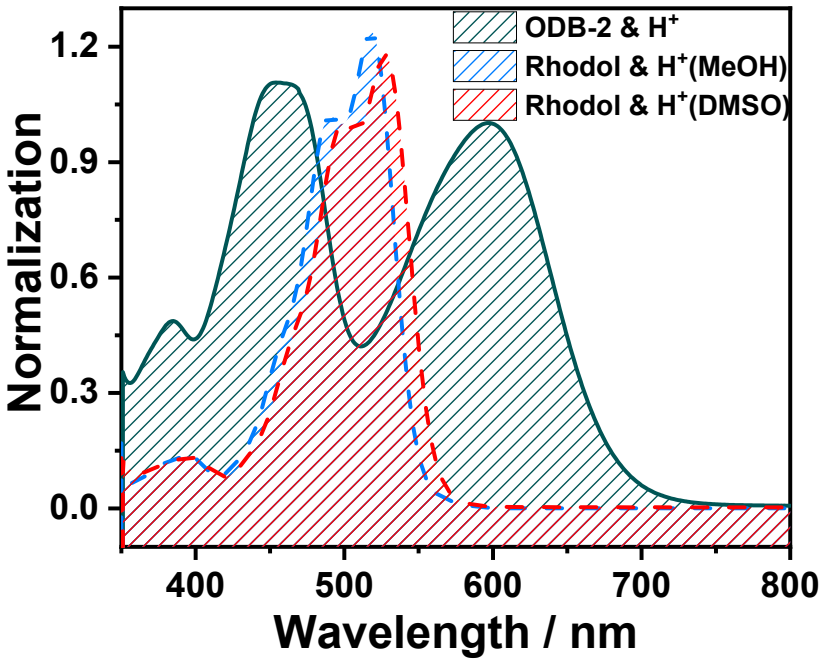

Fig. S2 Normalized UV–vis spectra of Rhodol & H^+ (MeOH, DMSO) and ODB-2 & H^+ (MeOH).

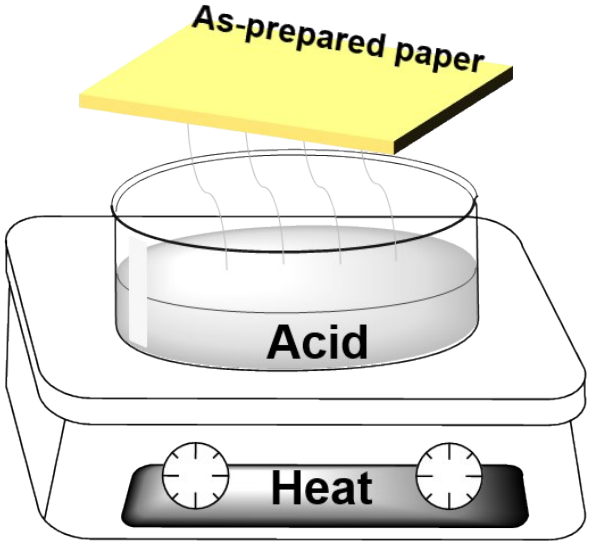

Fig. S3 Schematic illustrations of adding acid in as-prepared paper (The as-prepared paper was test after enough time fumigation by acid, and the paper has the darkest colour and colour-changed no longer with fumigation time increased).

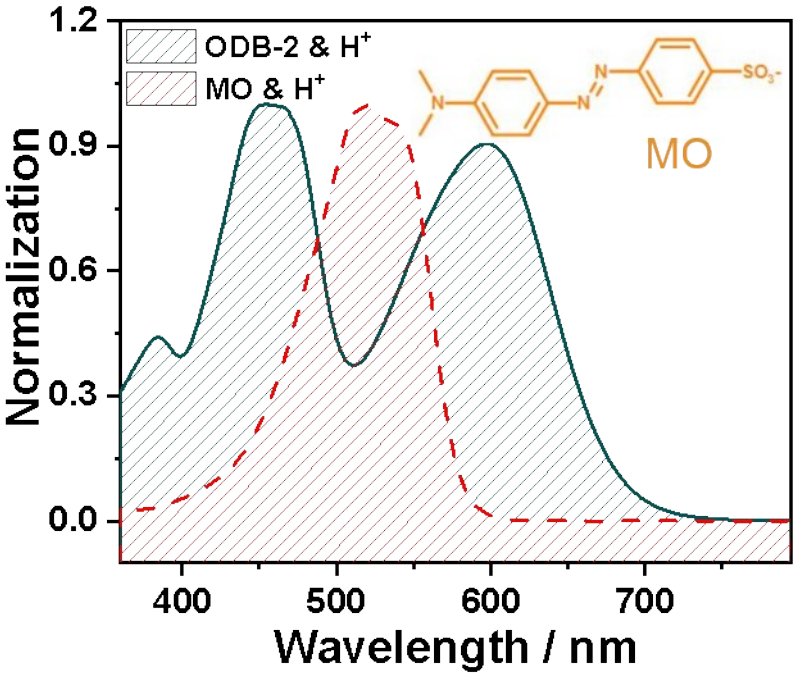

Fig. S4 Normalized UV–vis spectra of MO & H^+ and ODB-2 & H^+ in MeOH.

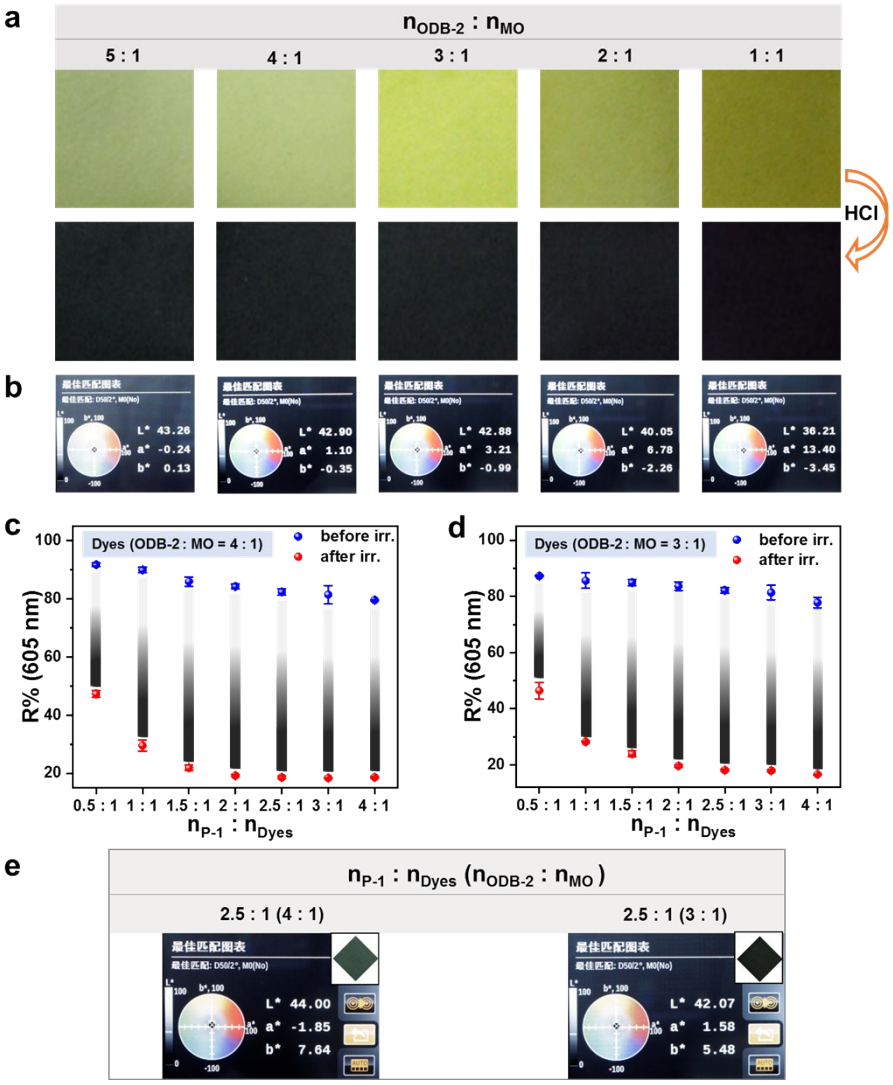

Fig. S5 (a) Photographs of papers loaded with different ratios of MO to ODB-2 (2.5 mM) before and after addition HCl. (b) L*, a*, b* measured by spectrodensitometer and photographs of papers loaded with different ratios of MO to ODB-2 (2.5 mM) after addition HCl. (c, d) Reflectance change at 605 nm of dyes & P-1 based paper with different ratio of P-1 and dyes before and after irradiation, which has different ratio of ODB-2 to MO: c) 4 / 1; d) 3 / 1. (e) L*, a*, b* measured by spectrodensitometer and photographs of P-1 & dyes (n/n 2.5/1) based paper after irradiation with different ratio of ODB-2 to MO: 4/1 (left);

3/1 (right).

4. References

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