

Supporting information

Black Hydrochromic Fluorane Molecular Switches: Substituent Positional Isomerization Effects and Multicolor Water-Jet Printing

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Methods

1. Materials and Instruments

The chemical agents and solvents used hereon were purchased from Adamas, Energy Chemical and Aladdin. **Acetonitrile** (CH₃CN, HPLC) were purchased from Yuwang Group (Shandong, China). Unless otherwise noted, other solvents and reagents were purchased in analytical grade and used without further purification. Deionized water (H₂O) was purified by Milli-Q system. 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) is selected as the paper substrate.

¹H NMR (400 MHz) and ¹³C NMR (101 MHz) spectra were measured in deuterated dimethyl sulfoxide (DMSO-d₆) on Bruker AVANCE400 using residual solvent peak as an internal reference. LC-HRMS analysis was performed on an Agilent 1290-micro TOF-Q II mass spectrometer. Melting point was determined using a SGW X-4B microscopy melting point apparatus (Shanghai, China). Absorption spectra were measured using a Shimadzu UV-2550 PC double-beam spectrophotometer (path length was 1 cm). Reflective UV/vis spectroscopy and in situ kinetic measurement was tested via reflective mode of integrating sphere on Analytik Jena Specord®210 plus UV/vis spectrophotometer, using barium sulfate as background.

2. Synthesis and Characterization

General procedure for the synthesis of *o*- / *m*- / *p*-NO₂-ODB-2: A solution of 3-(dibutylamino)phenol (13.28 g, 60 mmol) in toluene (120 mL) was added to nitrophthalic anhydride (11.59 g, 60 mmol). The reaction mixture was stirred for 5 h under reflux then cooled to room temperature. The reaction mixture was concentrated under reduced pressure. Then column chromatography was performed using dichloromethane/methanol as eluent to afford the two nitro keto-acid mixture as dark yellow solid (yield: *ca.* 59 %). To a flask charged with concentrated sulfuric acid (30 mL) was added nitro keto-acid (7.75 g) slowly

under argon. The flask was put into ice-water bath and then 4-methoxy-2-methyl-N-phenylaniline (1.93g, 10 mmol) was added slowly. The reaction mixture was stirred at room temperature for one day. The reaction mixture was transferred to ice-water by dropping to give a precipitate. Filtered to get the precipitate and washed with cold water. The precipitate was transferred to a beaker and dispersed with water, and the dispersion was neutralized with 10 wt % sodium hydrate. Extract the dispersion with dichloromethane, dry over anhydrous sodium sulfate, and concentrate at reduced pressure, the mixture was purified by column chromatography on silica gel to give the desired compounds.

3'-Nitro-2-phenylamino-3-methyl-6-dibutylaminofluoran (*o*-NO₂-ODB-2).

The mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 8 : 1) to afford yellow-green solid (346 mg, yield: 21%). Mp: 224.2 °C - 224.6 °C. ¹H NMR (400 MHz, DMSO-d₆) δ 8.17 (d, J = 7.8 Hz, 1H), 8.00 (t, J = 7.8 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.45 (s, 1H), 7.28 (s, 1H), 7.03 (t, J = 7.7 Hz, 2H), 6.68 - 6.60 (m, 2H), 6.56 - 6.51 (m, 3H), 6.48 - 6.42 (m, 2H), 3.33 - 3.25 (m, 4H), 2.21 (s, 3H), 1.55 - 1.45 (m, 4H), 1.38 - 1.27 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H). ¹³C NMR (101 MHz, DMSO-d₆) δ 163.33, 154.54, 152.40, 149.89, 146.65, 145.64, 145.25, 137.15, 137.07, 135.63, 128.85, 128.56, 124.63, 119.70, 118.77, 118.45, 117.71, 115.72, 114.69, 108.73, 102.73, 96.93, 83.36, 49.87, 28.86, 19.62, 17.91, 13.85. LC-HRMS (ESI) calcd. for C₃₅H₃₆N₃O₅ [M+H]⁺: 578.2649, found: 578.2649.

4'-Nitro-2-phenylamino-3-methyl-6-dibutylaminofluoran (*m*-NO₂-ODB-2).

The mixture was purified by column chromatography on silica gel (petroleum ether / ethyl acetate = 10 : 1) to afford green solids (277 mg, yield: 16%). Mp: 108.7 °C - 109.5 °C. ¹H NMR (400 MHz, DMSO-d₆) δ 8.62 (s, 1H), 8.57 (dd, J = 8.4, 1.7 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.43 (s, 1H), 7.29 (s, 1H), 7.01 (t, J = 7.7 Hz, 2H), 6.65 - 6.56 (m, 2H), 6.55 - 6.48 (m, 3H), 6.46 - 6.39 (m, 2H), 3.33 - 3.21 (m, 4H), 2.20 (s, 3H), 1.55 - 1.45 (m, 4H), 1.37 - 1.26 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H). ¹³C NMR (101 MHz, DMSO-d₆) δ 166.71, 157.47, 152.28, 149.93, 149.11,

146.61, 145.38, 137.03, 135.97, 130.40, 128.91, 127.61, 125.97, 120.18, 120.15, 118.82, 118.40, 115.62, 114.54, 108.70, 102.63, 96.95, 84.25, 49.89, 28.89, 19.66, 17.96, 13.90. LC-HRMS (ESI) calcd. for $C_{35}H_{36}N_3O_5$ $[M+H]^+$: 578.2649, found: 578.2648.

5'-Nitro-2-phenylamino-3-methyl-6-dibutylaminofluoran (*p*-NO₂-ODB-2).

The mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10 : 1) to afford orange solid (329 mg, yield: 19%). mp: 92.8 °C - 93.6 °C. ¹H NMR (400 MHz, DMSO-d₆) δ 8.46 (dd, J = 8.4, 1.9 Hz, 1H), 8.21 (d, J = 8.4, 1H), 8.17 (s, 1H), 7.41 (s, 1H), 7.28 (s, 1H), 6.98 (t, J = 7.8 Hz, 2H), 6.65 - 6.57 (m, 2H), 6.54 (d, J = 7.8 Hz, 2H), 6.48 (s, 1H), 6.46 - 6.38 (m, 2H), 3.33 - 3.26 (m, 4H), 2.21 (s, 3H), 1.55 - 1.45 (m, 4H), 1.38 - 1.27 (m, 4H), 0.91 (t, J = 7.3 Hz, 6H). ¹³C NMR (101 MHz, DMSO-d₆) δ 166.86, 153.31, 152.53, 152.49, 149.89, 146.62, 145.22, 137.00, 135.46, 130.99, 128.94, 128.84, 126.67, 125.59, 119.52, 119.46, 118.81, 118.48, 115.71, 114.73, 108.61, 102.78, 96.97, 84.40, 49.91, 28.90, 19.66, 17.96, 13.90. LC-HRMS (ESI) calcd. for $C_{35}H_{36}N_3O_5$ $[M+H]^+$: 578.2649, found: 578.2648.

The detailed NMR and LC-MS spectra of *o*- / *m*- / *p*-NO₂-ODB-2 are shown in **Fig. S2–S16**.

3. Preparation of *o*- / *m*- / *p*-NO₂-ODB-2-HM

The hydrochromic materials (HMs) integrated with *o*-/*m*-/*p*-NO₂-ODB-2 was prepared in a layer-by-layer manner, which referred to our previous work¹. The filter paper substrate was coated with a layer of 10 wt % PEG aqueous solution and dried at 90 °C. Then *N,N*-Dimethylformamide (DMF) /H₂O (10/1 by volume) solution of *o*- / *m*- / *p*-NO₂-ODB-2 (0.02 mol/L) containing 1 wt% PEG is coated over the initial PEG layer, and dried at 90 °C.

4. Preparation of water-jet rewritable papers (WJRPs)

The WJRPs integrated with *o*-NO₂-ODB-2 was prepared in a layer-by-layer manner. The filter paper substrate was coated with a layer of 10 wt % PEG aqueous solution and dried at 90 °C. Then DMF/H₂O (10/1 by volume) solution

of *o*-NO₂-ODB-2 (0.02 mol/L) and various surfactants aqueous solution (0.1 mol/L) containing 1 wt% PEG is coated over the PEG layer, and dried at 90 °C.

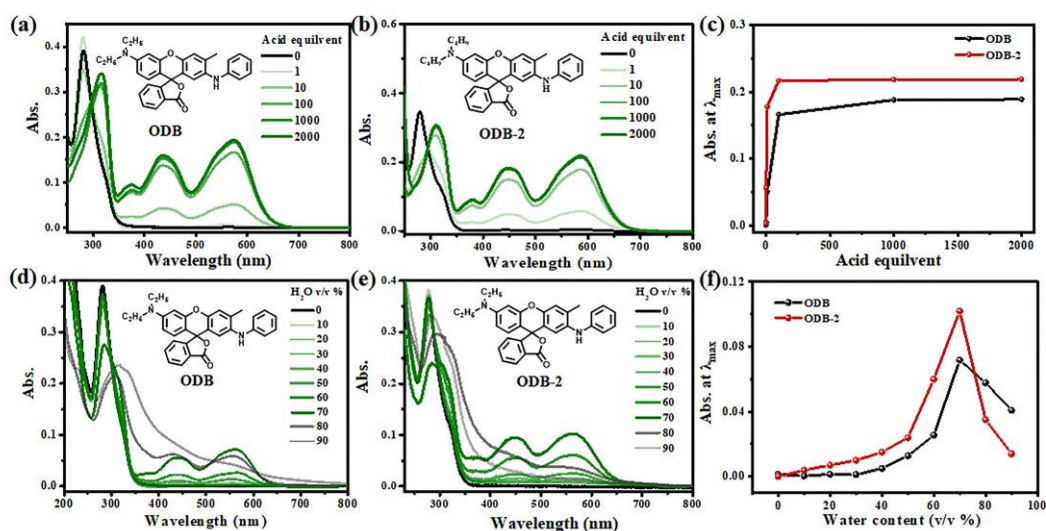


Fig. S1 UV/vis absorption spectrum of (a, d) ODB-1 and (b, c) ODB-2 in MeCN solution (1×10^{-5} mol/L) with different equivalent of CF₃COOH and MeCN-H₂O binary solutions (1×10^{-5} mol/L) with increasing percentage of water by volume from 0 to 90% and in MeCN-H₂O binary solutions with water content of 70% after adding CF₃COOH. Plots of absorbance at long absorption peak for ODB-1 and ODB-2 in (f) MeCN solution with different equivalent of CF₃COOH and (f) MeCN-H₂O binary solutions with increasing percentage of water by volume from 0 to 90%.

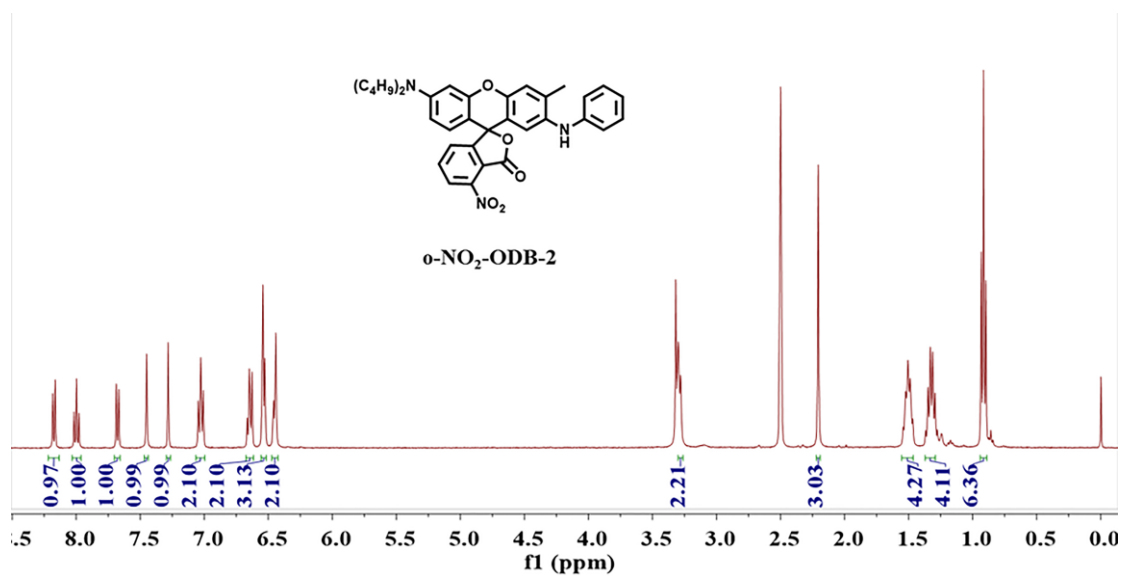


Fig. S2 ¹H-NMR spectrum of *o*-NO₂-ODB-2 in deuterated dimethyl sulfoxide (DMSO-*d*₆) (400 MHz).

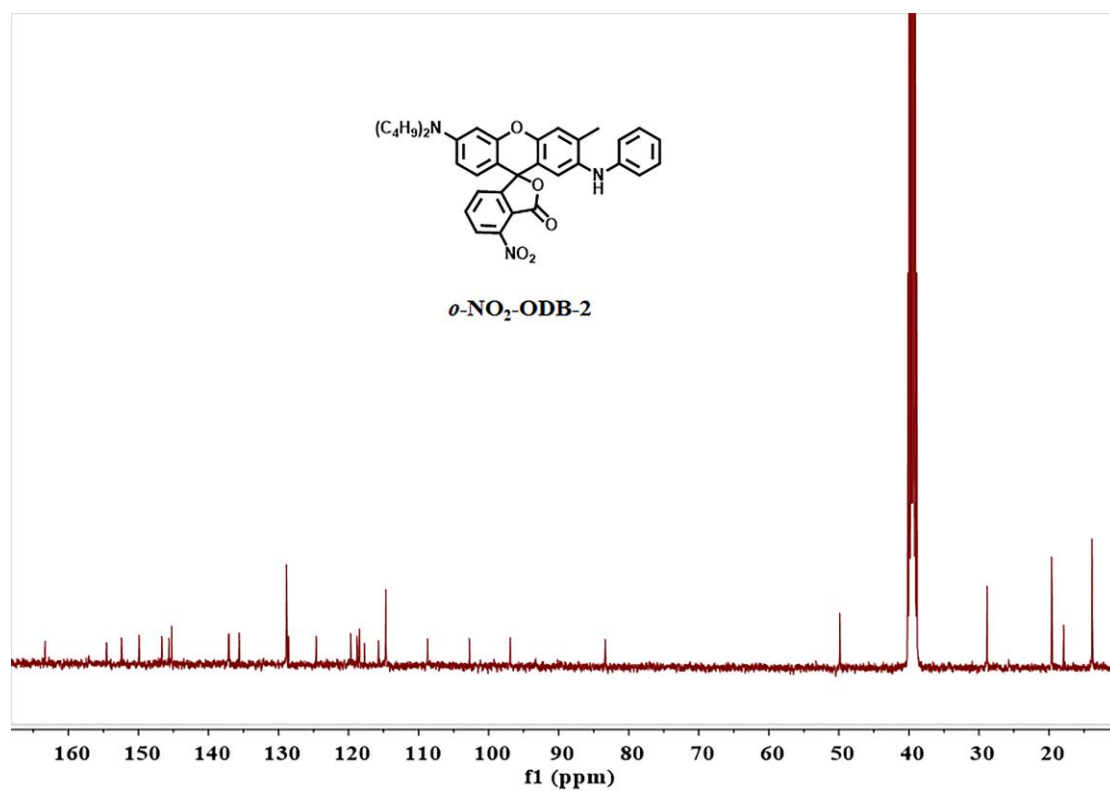


Fig. S3 ¹³C-NMR spectrum of *o*-NO₂-ODB-2 in DMSO-*d*₆ (400 MHz).

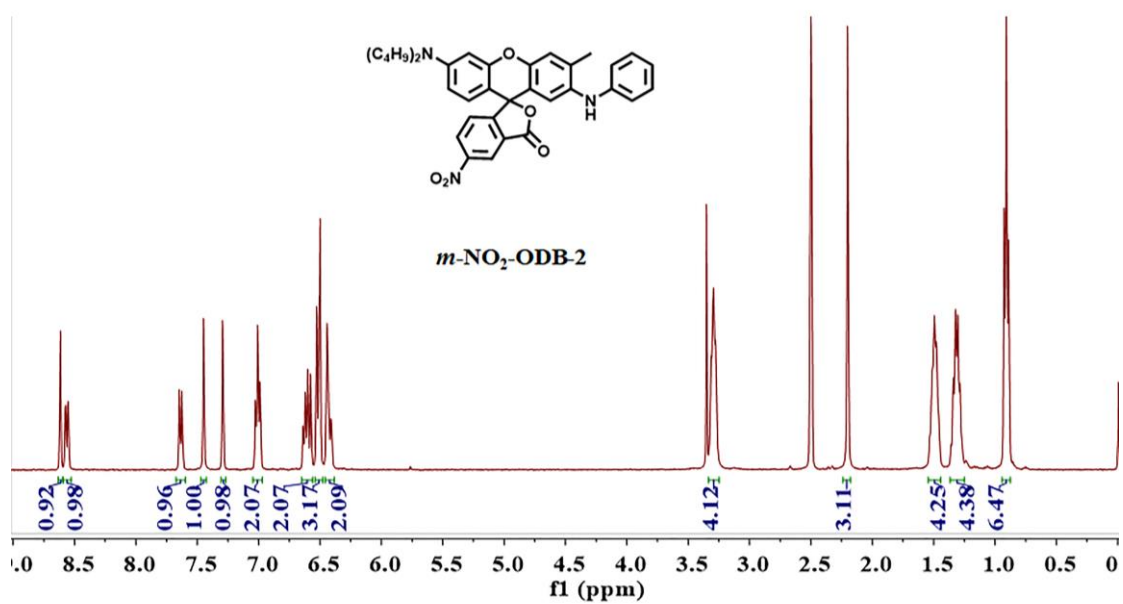


Fig. S4 ¹H-NMR spectrum of *m*-NO₂-ODB-2 in DMSO-*d*₆ (400 MHz).

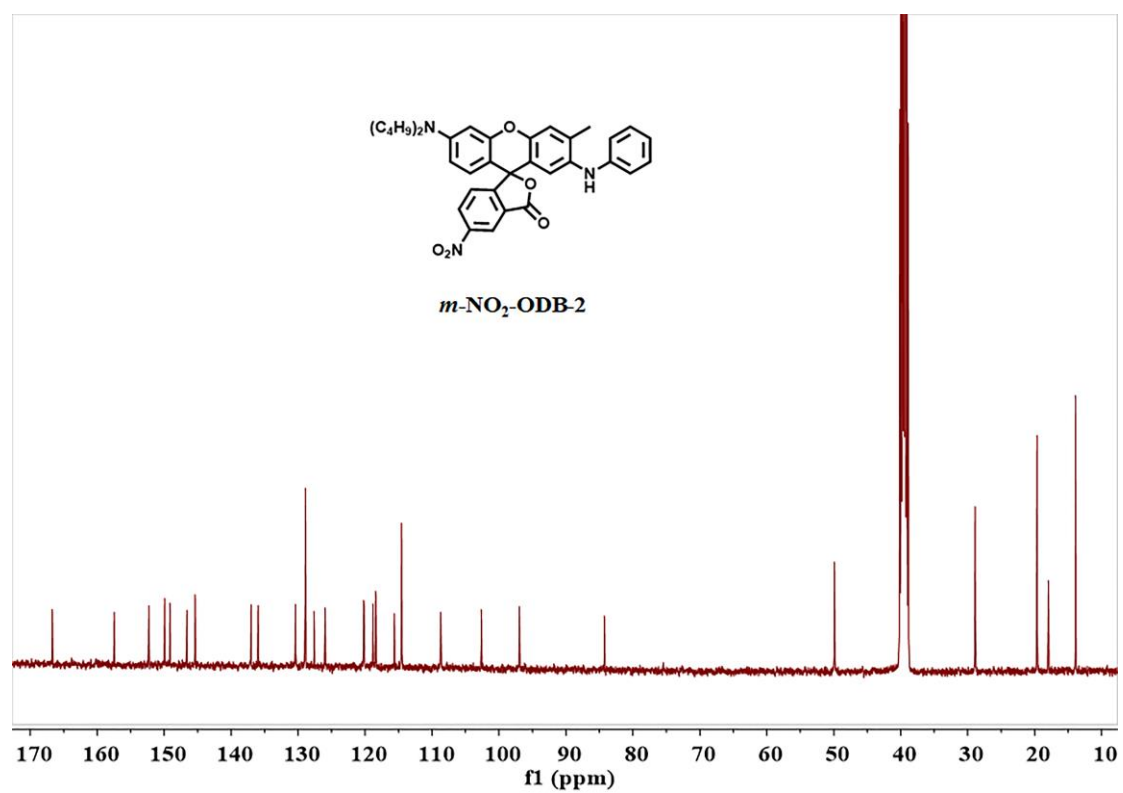


Fig. S5 ¹³C-NMR spectrum of *m*-NO₂-ODB-2 in DMSO-*d*₆ (400 MHz).

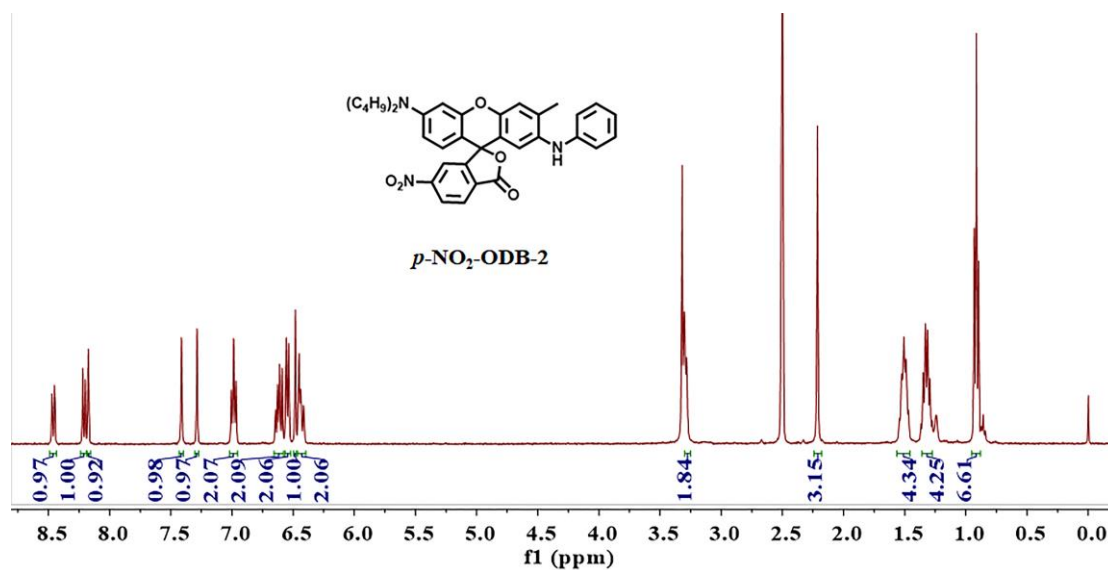


Fig. S6 ¹H-NMR spectrum of *p*-NO₂-ODB-2 in DMSO-*d*₆ (400 MHz).

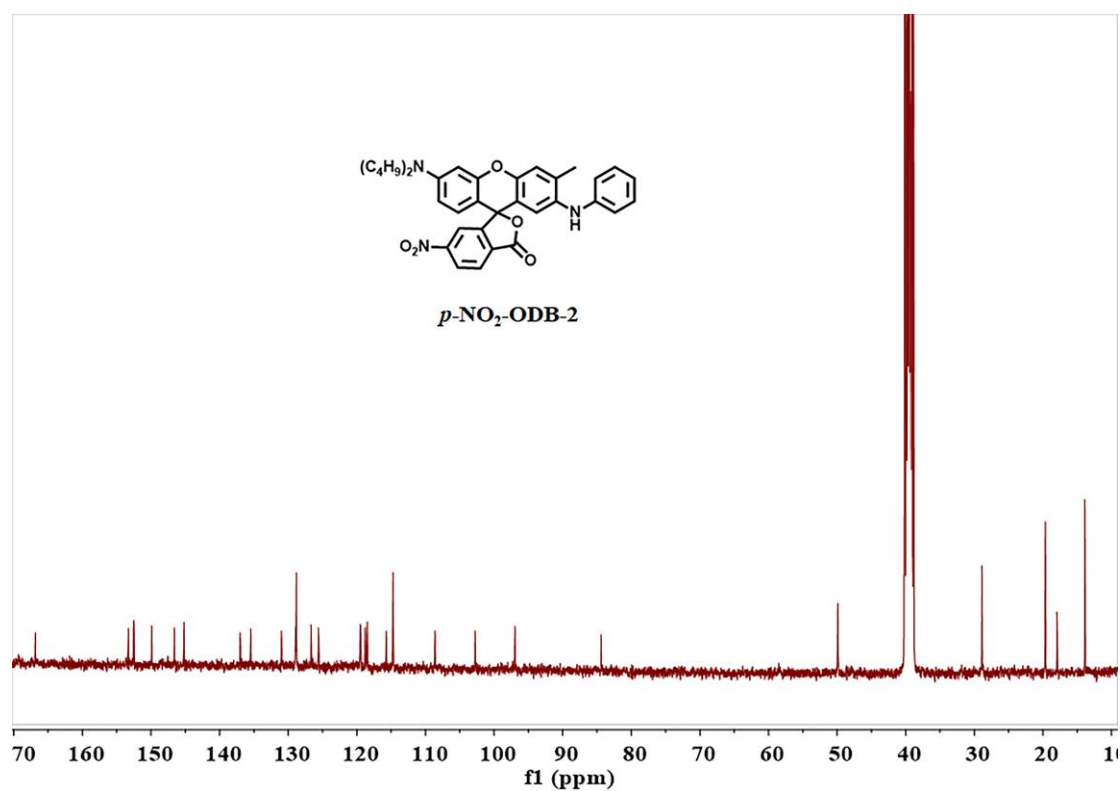


Fig. S7 ¹³C-NMR spectrum of *p*-NO₂-ODB-2 in DMSO-*d*₆ (400 MHz).

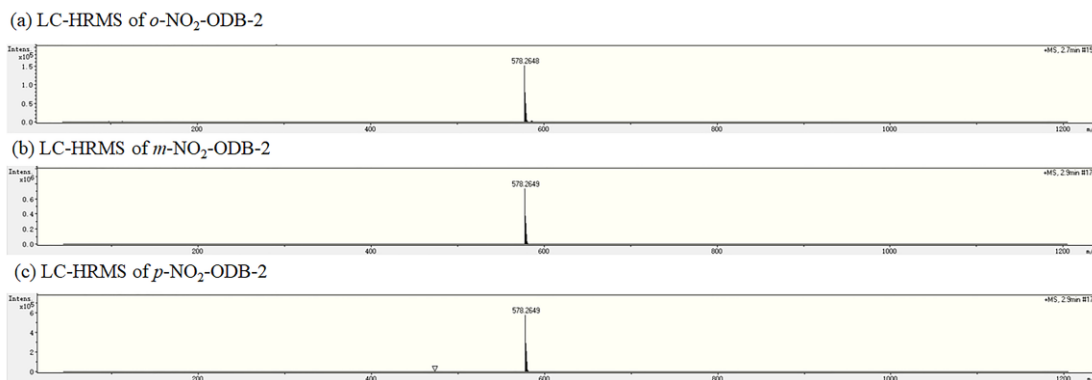


Fig. S8 LC-HRMS spectra of (a) *o*-NO₂-ODB-2, (b) *m*-NO₂-ODB-2, (c) *p*-NO₂-ODB-2.

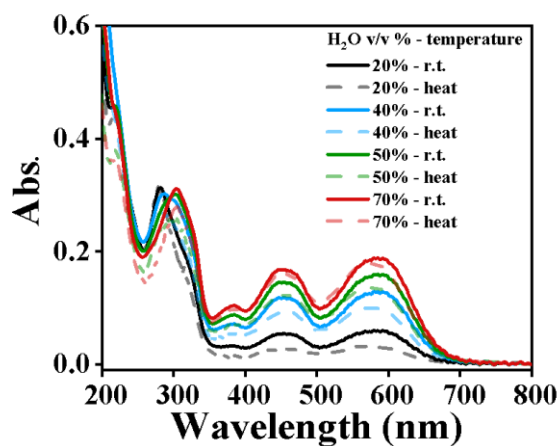


Fig. S9 UV/vis absorption spectra of *o*-NO₂-ODB-2 in MeCN-H₂O binary solutions (1×10^{-5} mol/L) with water contents of 20%, 40% and 60% (by volume) under room temperature (r. t.: 23.7 °C) and heat (75 ± 2 °C), respectively.

As shown in **Fig. S9**, after the solutions of *o*-NO₂-ODB-2 in MeCN-H₂O with different H₂O contents (20%, 40%, 70%) were heated (70 °C), their absorbance(s) at 400-600 nm all decreased relative to their absorbance(s) at room temperature (dotted lines vs. solid lines). This result indicates that the proportion of the open form of *o*-NO₂-ODB-2 was decreased. This is mainly because high temperature destroys the hydrogen bonding between H₂O and the open form of *o*-NO₂-ODB-2, which weakens the stabilizing effect of H₂O on the open form of *o*-NO₂-ODB-2. And this weakening effect is more obvious with less water content.

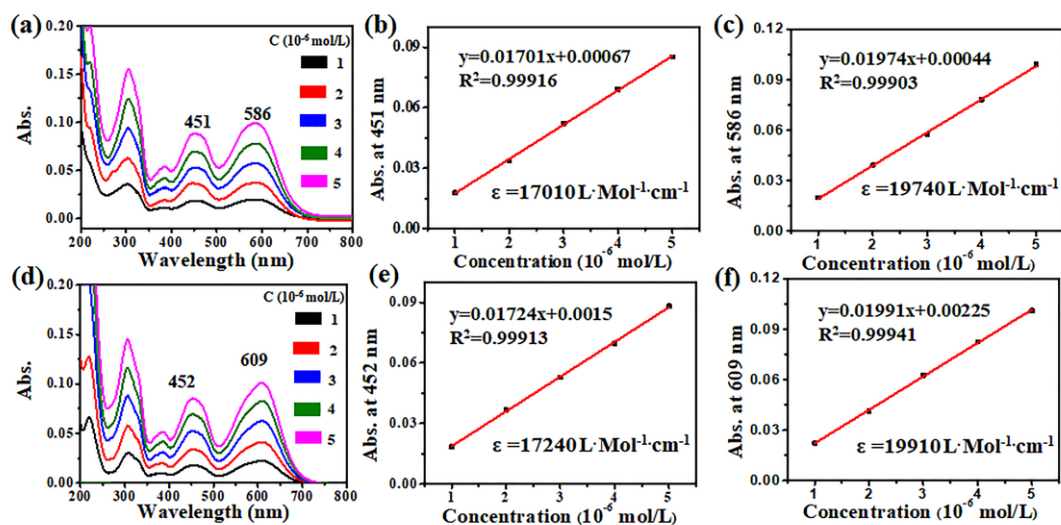


Fig. S10 UV/vis absorption spectra of *o*-NO₂-ODB-2 in MeCN/H₂O (v/v 3/7) with different concentrations (the maximum ring-open form of *o*-NO₂-ODB-2 is reached which was checked by adding acid) and thus its hydrochromic (a-c) and acidichromic (d-f) molar absorption coefficients (ϵ) at λ_{\max} was obtained according to Lambert-Beer law.

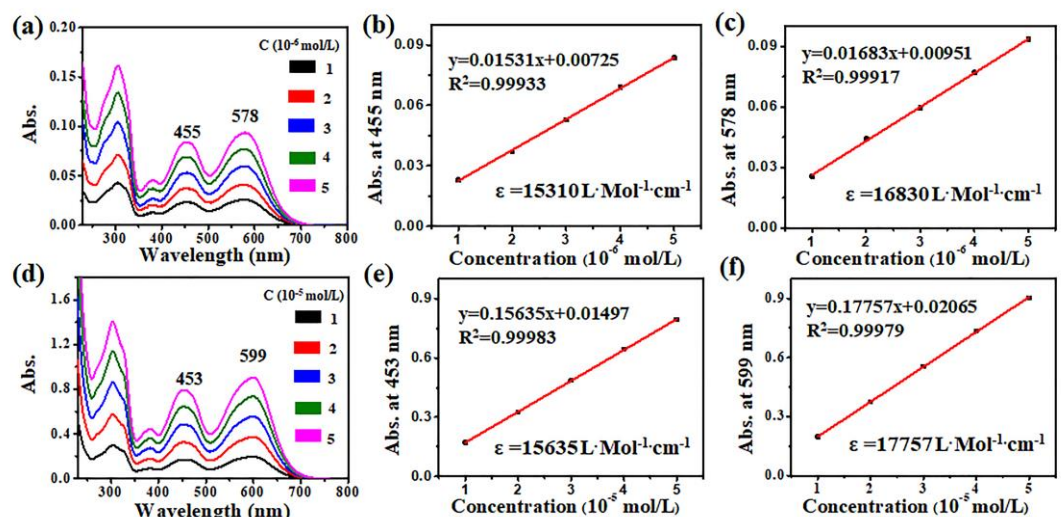


Fig. S11 UV/vis absorption spectra of *m*-NO₂-ODB-2 in MeCN/H₂O (v/v 3/7) with different concentrations (the maximum ring-open form of *m*-NO₂-ODB-2 is reached which was checked by adding acid) and thus its hydrochromic (a-c) and acidichromic (d-f) molar absorption coefficients (ϵ) at λ_{\max} was obtained according to Lambert-Beer law.

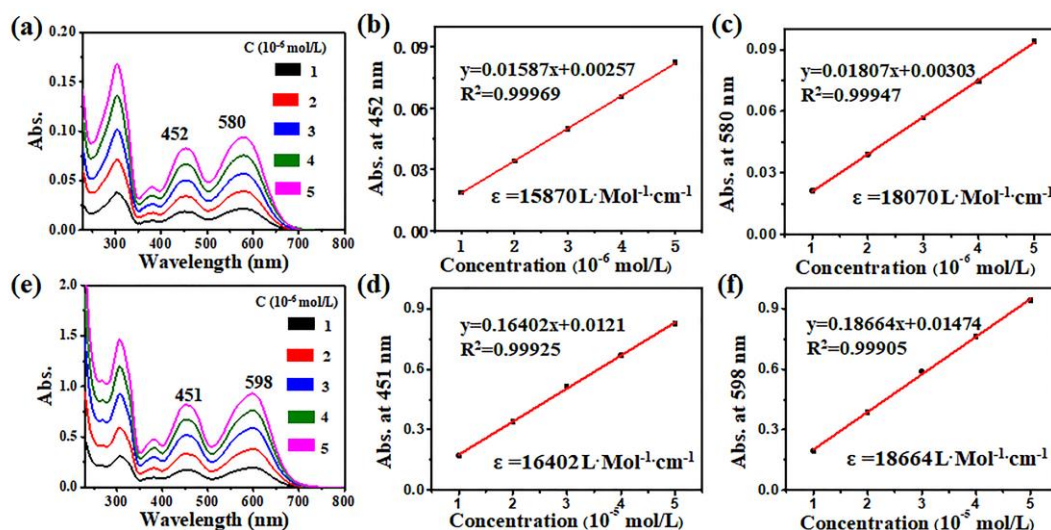


Fig. S12 UV/vis absorption spectra of *p*-NO₂-ODB-2 in MeCN/H₂O (v/v 3/7) with different concentrations (the maximum ring-open form of *p*-NO₂-ODB-2 is reached which was checked by adding acid) and thus its hydrochromic (a-c) and acidichromic (d-f) molar absorption coefficients (ϵ) at λ_{\max} was obtained according to Lambert-Beer law.

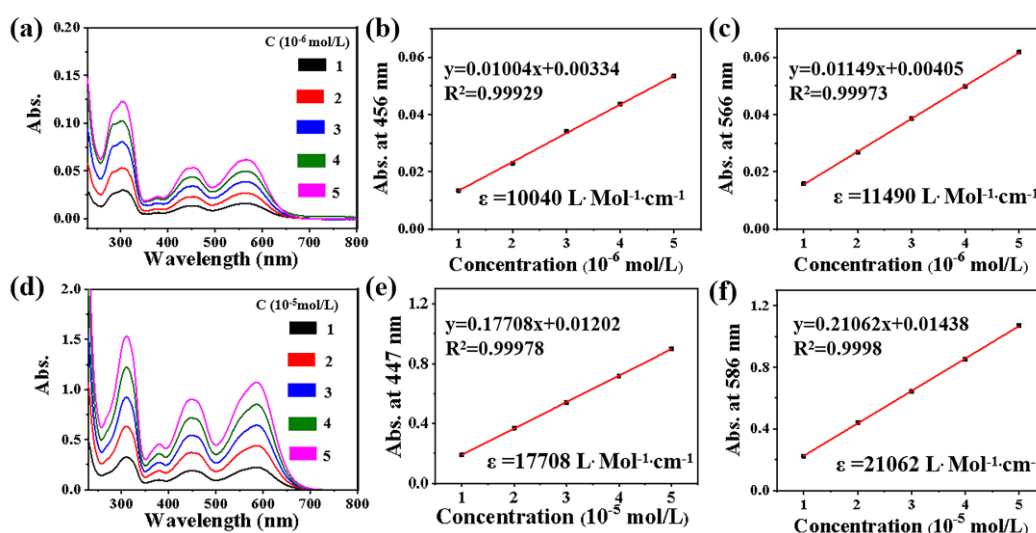


Fig. S13 UV/vis absorption spectra of ODB-2 in MeCN/H₂O (v/v 3/7) with different concentrations (the maximum ring-open form of ODB-2 is reached which was checked by adding acid) and thus its hydrochromic (a-c) and acidichromic (d-f) molar absorption coefficients (ϵ) at λ_{\max} was obtained according to Lambert-Beer law.

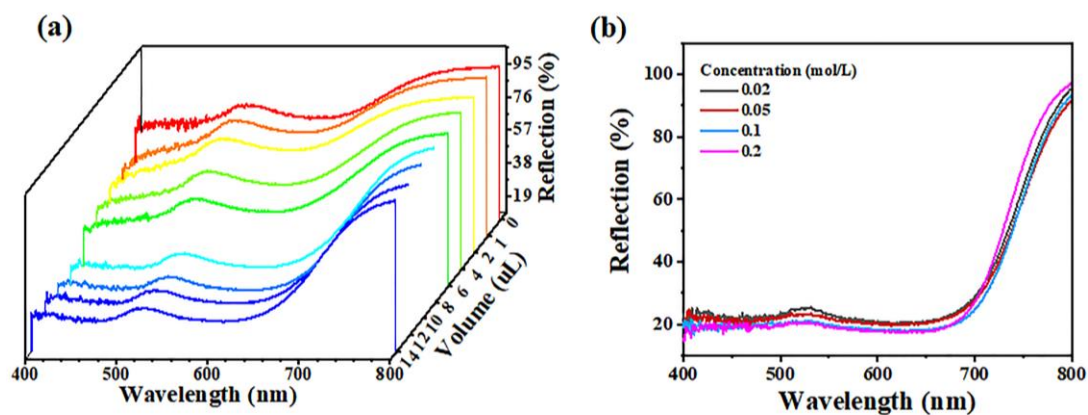


Fig. S16 The UV-vis reflection spectra of *o*-NO₂-ODB-2-HM in 1 cm² area after exposure to (a) different volume of water and with (b) different concentration.

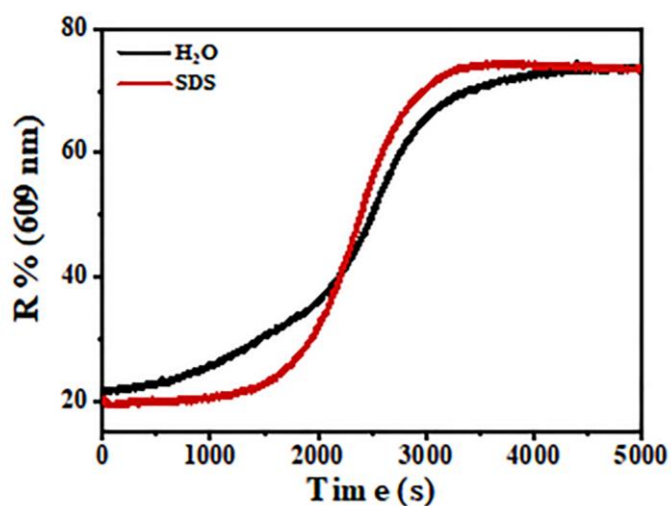


Fig. S17 Time-dependent reflection variations of the *o*-NO₂-ODB-2-HM in 1 cm² area of at 609 nm after the same amount (10 μL) of water (black line) and SDS aqueous solution (red line).

Table S1 L^* , a^* , b^* values of WJRPs based on the ODB-2 derivatives before and after different stimuli.

Hydrochromic systems	Stimulate	L^*	a^*	b^*
	--	87.01	-3.43	8.85
<i>o</i> -NO ₂ -ODB-2	water	45.71	-7.66	4.17
	SDS aq.	22.62	-1.79	-0.63
Black ink	--	30.41	0.76	1.91

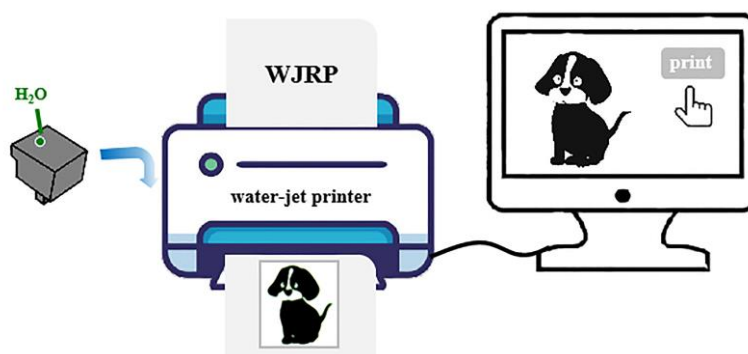


Fig. S18 Schematic representation of the water-jet rewritable application on *o*-NO₂-ODB-2 based paper.

References

S1 L. Sheng, M. Li, S. Zhu, H. Li, G. Xi, Y. Li, Y. Wang, Q. Li, S. Liang, K. Zhong, S. X.-A. Zhang, *Nat. Commun.* 2014, **5**, 3044.