

## Supporting Information

New absorption/fluorescence dual-mode hydrochromic dye and its applications for water-jet printing and anti-counterfeiting

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## 1. Experimental section

**Materials.** Lithium Aluminium Hydride ( $\text{LiAlH}_4$ , 98%), rhodamine B hydrochloride (95%), Phosphorus oxychloride (99.5%), *n*-Propylamine (99%) were purchased from Energy Chemical Company (Shanghai, China). PEG 20000 (molecular weight: 17,000-22,000) was purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). Cellulose filter paper was purchased from General Electric Biotechnology Company (grade 102, Hangzhou, China), and was selected as the paper substrate. All of the solvents were purchased from Beijing Chemical Works.

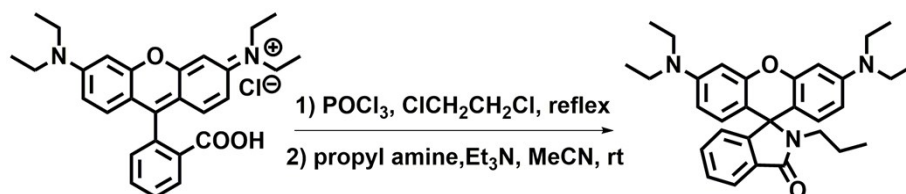
**Instrument.** Absorption spectra were measured by using a Shimadzu double-beam UV-2550 PC spectrophotometer. Reflective UV-vis spectroscopy of water-jet rewritable paper (**WJRP**) before and after addition of water was tested via reflective mode of integrating sphere on Analytik Jena Specord®210 plus UV/Vis spectrophotometer,  $\text{BaSO}_4$  was chosen as the background, the path length was 1 cm. Fluorescence measurements were carried out on a Shimadzu RF5301 PC fluorescence spectrometer. Microscale colors of the WJRP were imaged in transmission/reflective and fluorescence modes using Leica DM4000 M microscope.  $^1\text{H}$  NMR (500 MHz) and  $^{13}\text{C}$  NMR (126 MHz) spectra were recorded on a Bruker AVANCE 500 at room temperature. LC-HRMS analysis was performed on an Agilent 1290-micro TOF-Q II mass spectrometer. Melting point was measured by using a SGW X-4B microscopy melting point measuring instrument.

**Preparation of WJRPs.** The WJRPs integrated with **Pr-N-RhB** were prepared via a layer-by-layer coating method, which referred to our reported work.<sup>S1</sup> The filter paper substrate was coated with a layer of 10 wt% PEG aqueous solution and dried out at 80 °C. WJRPs with dissolving solvent of EtOH- $\text{H}_2\text{O}$ : **Pr-N-RhB** ( $1 \times 10^{-4}$  M) in EtOH mixed with 10 % PEG in  $\text{H}_2\text{O}$  (20:1, v/v), then the mixed solution coated over the initial PEG layer and dried at 80 °C.

## 2. Preparation and synthesis

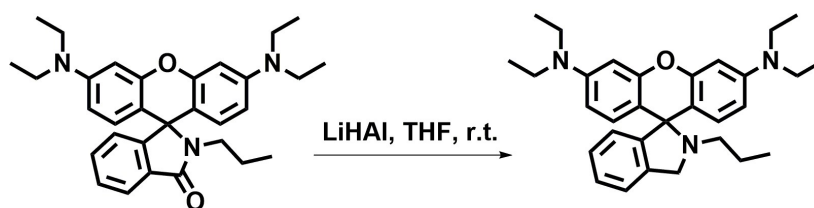
**NH<sub>2</sub>-RhB** and **RhB (lactone form)** were prepared according to our previous work<sup>S2</sup>.

**Pr-CO-N-Rh** was prepared according to reported method<sup>S3</sup>.



Scheme S1. Synthesis of **Pr-CO-N-Rh**

**Synthesis of Pr-CO-N-RhB.** To a solution of rhodamine B hydrochloride (2.0 g, 4.5 mmol) in 1,2-dichloroethane (25 mL) at room temperature, phosphorus oxychloride ( $\text{POCl}_3$ ) (2.5 mL, 27 mmol) was added dropwise. The mixture was kept stirred at 80 °C for 6 hours and then cooled to room temperature and concentrated under vacuum to remove the 1,2-dichloroethane, purple viscous solid was obtained. Under the ice water bath, the purple viscous solid was dissolved in anhydrous acetonitrile (MeCN) (10 mL), then the solution was added dropwise to an anhydrous MeCN (5 mL) solution containing propyl amine (0.42 mL, 5 mmol) and triethylamine (8 mL). The mixture was stirred at room temperature for 7 h. After that it was concentrated under vacuum and **Pr-CO-N-RhB** was purified (2.13 g, 88 % yield) by column chromatography on silica gel (n-hexane / ethyl acetate = 12 : 1).  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  7.77 (m, 1H), 7.49 (p,  $J = 6.7$  Hz, 1H), 7.01 (m, 1H), 6.33 (dd,  $J = 28.1, 9.7$  Hz, 6H), 3.32 (q,  $J = 6.8$  Hz, 8H), 2.94 - 2.87 (m, 2H), 1.08 (m, 14H), 0.59 (t,  $J = 7.3$  Hz, 3H) ppm.



**Scheme S2.** Synthesis of **Pr-N-RhB**

**Synthesis of Pr-N-RhB.** **Pr-CO-N-RhB** (1 g, 2.1 mmol) was dissolved in 10 ml tetrahydrofuran (THF),  $\text{LiAlH}_4$  was added slowly to the solution, the obtained mixture was stirred for 6 h under the room temperature. After that 0.5 ml  $\text{H}_2\text{O}$  was added. The solution was extracted by ethyl acetate (20 ml  $\times$  3) and the organic layer was washed by 15 % NaOH aqueous solution. Then the organic layer was collected and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . Crude product was obtained after filtration and concentration, and then was purified by chromatography on silica gel (n-hexane / ethyl acetate = 8 : 1) to afford **Pr-N-RhB** as a pink solid (0.68 g, 69 % yield). Melt point: 131.7-132.5 °C.  $^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$  7.37 (d,  $J = 7.5$  Hz, 1H), 7.23 (t,  $J = 7.4$  Hz, 1H), 7.14 (t,  $J = 7.4$  Hz, 1H), 6.67 (d,  $J = 7.5$  Hz, 1H), 6.56 (d,  $J = 8.7$  Hz, 2H), 6.32 (dd,  $J = 8.8, 2.1$  Hz, 2H), 6.27 (d,  $J = 2.1$  Hz, 2H), 4.13 (s, 2H), 3.30 (dd,  $J = 13.0, 6.0$  Hz, 8H), 2.08 (t,  $J = 7.2$  Hz, 2H), 1.35 - 1.26 (m, 2H), 1.08 (t,  $J = 6.9$  Hz, 12H), 0.64 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ )  $\delta$  152.7, 150.2, 147.8, 139.0, 130.6, 127.8, 127.1, 124.3, 122.6, 111.7, 107.7, 97.3, 67.7, 56.0, 50.3, 44.1, 22.1, 13.0, 12.2 ppm. LC-HRMS:  $m/z$  calculated for  $[\text{M} + \text{H}]^+$  470.3166, found 470.3154.

### 3. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

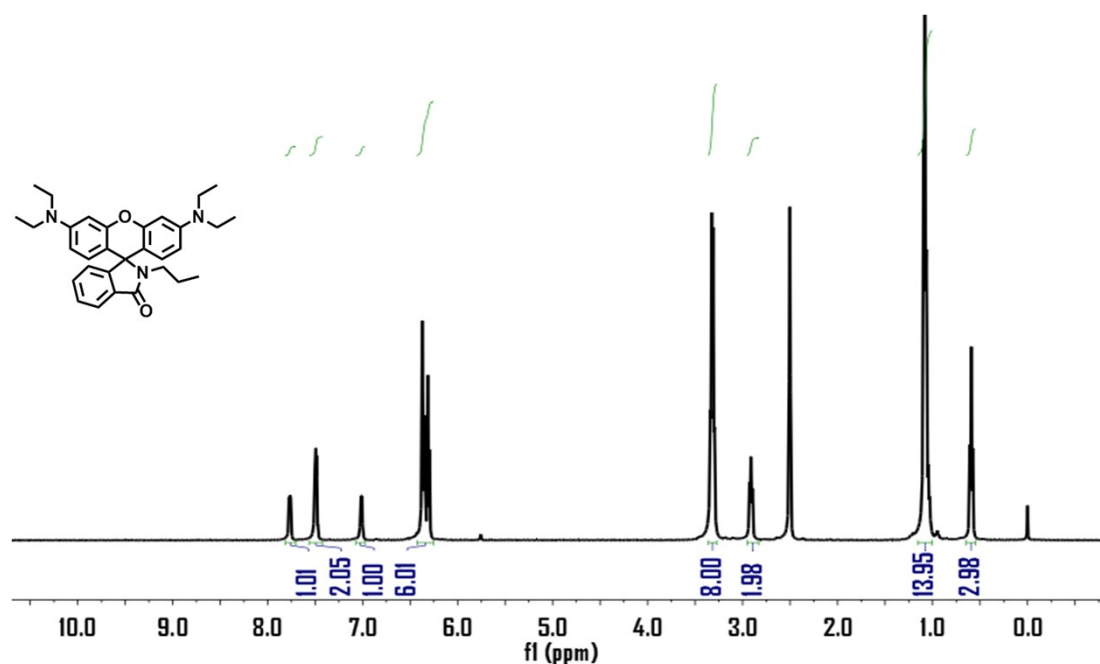


Fig. S1  $^1\text{H}$  NMR spectrum of Pr-CO-N-RhB in DMSO- $d_6$

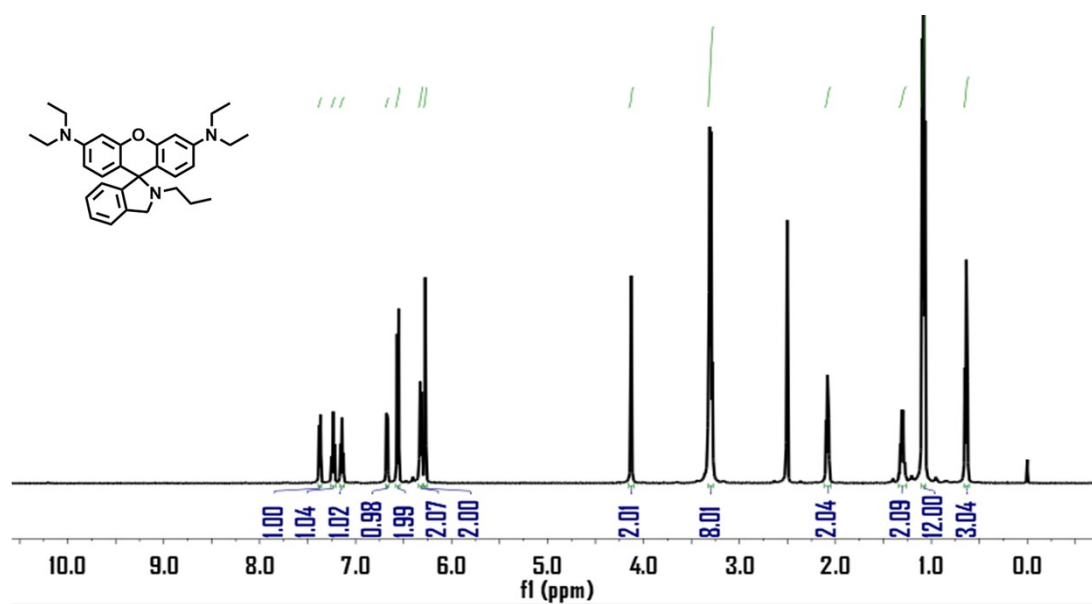


Fig. S2  $^1\text{H}$  NMR spectrum of Pr-N-RhB in DMSO- $d_6$

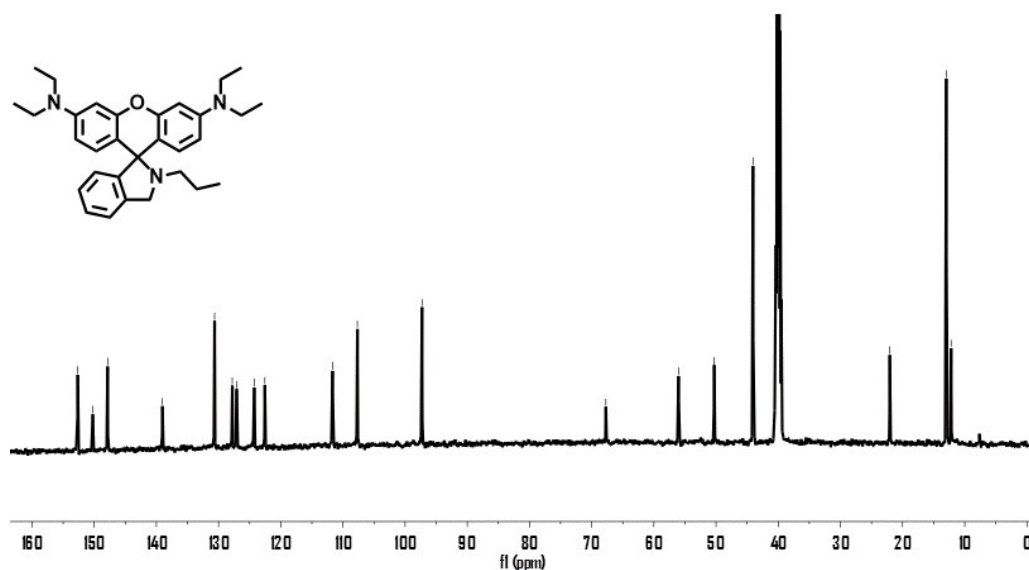


Fig. S3.  $^{13}\text{C}$  NMR spectrum of **Pr-N-RhB** in  $\text{DMSO-}d_6$

#### 4. Supplemental data

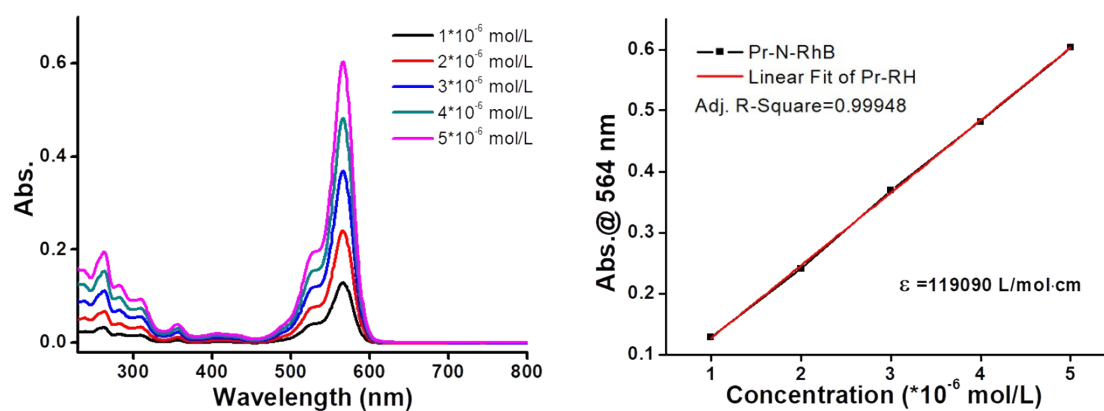
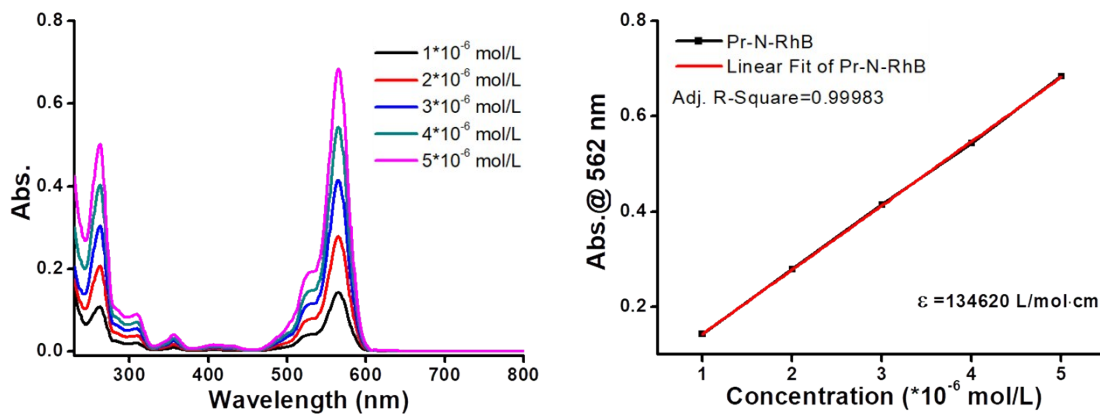
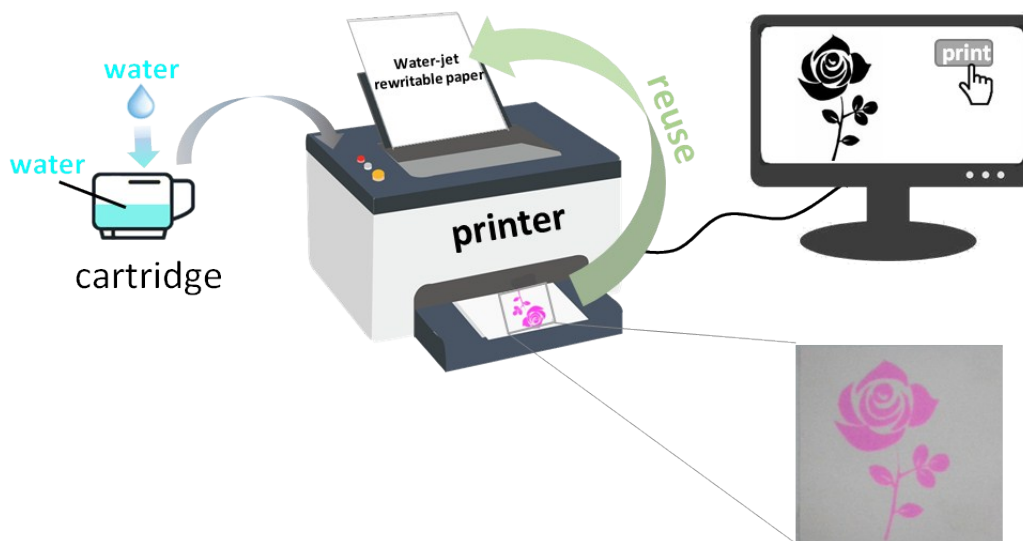


Fig. S4 Spectra of **Pr-N-RhB** in  $\text{MeCN}/\text{H}_2\text{O}$  (20/80 v/v%) with different concentrations (the maximum ring-open form of **Pr-N-RhB** is reached which was checked by adding acid) and thus its hydrochromic molar absorption coefficients ( $\epsilon$ ) at  $\lambda_{\text{max}}$  (i.e., 564 nm) was obtained according to Lambert-Beer law.



**Fig. S5** Spectra of **Pr-N-RhB** in MeCN with different concentrations after adding excess acid to reach its maximum ring-open form and thus its halochromic molar absorption coefficients ( $\epsilon$ ) at  $\lambda_{\text{max}}$  (i.e., 562 nm) was obtained according to Lambert-Beer law.



**Fig. S6** Schematic representation of the water-jet rewritable application on **Pr-N-RhB**-based paper.

## 5. References

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