Fluorane Salicylaldehyde Hydrazone Zn(II) Complex: Reversible Photochromic System both in Solution and in Solid Matrix

Yuanyuan Li,^{a,b} Kai Li,^{*b,c} Lili Wang,^b Yanling He,^b Juan He,^a Hongwei Hou^{*b} and Ben Zhong Tang^{*c}

^a College of Chemistry, Chemical and Environmental Engineering, Henan University of Technology, Henan 450001, P. R. China.

^b College of Chemistry and Molecular Engineering, Zhengzhou University, Henan 450001, P. R. China.

^c Department of Chemistry and Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China.

Contents

1.	Selected	spectra	and	data	referred	in	the
pape	r	••••••	S2				
2. Ca	ption of the vi	ideo	•••••	••••••	•••••	•••••	S4
3. NN	/IR spectra	•••••	•••••	•••••	•••••	•••••	
4. ES	I-MS spectra.			•••••	••••••		

1. Selected spectra and data referred in the paper

Wavelength / nm	365	400	425	450	475	500	550	600
Color change of 1-	Ye	Ye	Ye	No	No	No	No	No
Zn	S	S	S					
Color change of 2-	Ye	Ye	Ye	No	No	No	No	No
Zn	S	S	S					
Color change of 3-	Ye	Ye	Ye	No	No	No	No	No
Zn	S	S	S					

Table S1. The influence of light wavelengths on the color changes of 1-Zn, 2-Zn and 3-Zn.

Table S2. The fluorescence lifetimes and quantum yields fluorescence of 1-Zn, 2-Zn and 3-Zn in solution before and after UV light irradiation.

	Lifetime in DCM / ns		Quantum yield in DCM / %		
	Non-irradiated	Irradiated	Non-irradiated	Irradiated	
1-Zn	3.47	3.05	8.17	0.96	
2-Zn	3.21	3.06	18.36	6.98	
3-Zn	3.18	2.95	11.99	2.73	

Table S3. The fluorescence lifetimes and fluorescence quantum yields of 1-Zn, 2-Zn and 3-Zn in solid matrix before and after UV light irradiation.

	Lifetime	/ ns	Quantum yield / %		
	Non-irradiated	Irradiated	Non-irradiated	Irradiated	
1-Zn	1.69	1.59	3.55	1.21	
2-Zn	1.57	1.41	6.94	1.44	
3-Zn	1.56	1.46	5.70	1.07	



Figure S1. UV-Vis spectra titrations of the dyes of A) **1**, B) **2** and C) **3** to Zn(II) and their nonlinear fitting results. The absorbance wavelength was 615 nm, 494 nm and 585 nm, respectively. A0, AM, Ht and K in the figures represent the absorbance of dyes without Zn(II), the absorbance of dyes with excess Zn(II), the concentration of dyes and the binding constants between dyes and Zn(II), respectively. Conditions: $[1] = [2] = [3] = 500 \,\mu\text{mol/L}$, $[Zn(II)] = 0.750 \,\mu\text{mol/L}$. 2 mm quartz cells were used in the experiments.



Figure S2. Job's plot method for evaluating the stoichiometry of the complexes. A) **1** with Zn(II), B) **2** with Zn(II) and C) **3** with Zn(II). The absorbance wavelength was 615 nm, 494 nm and 585 nm, respectively. The total concentrations of dyes and Zn(II) were 500 μ mol/L. 2 mm quartz cells were used in the experiments.



Figure S3. The thermal recovery kinetics of **1-Zn** in different solvents at 20 °C. Inset: The curves were fitted with one-order reaction dynamics ($\ln A = -kt$). [**1**] = 500 µmol/L, [Zn(II)] = 5 mmol/L, $\lambda = 615$ nm.



Figure S4. The thermal recovery kinetics of **2-Zn** in different solvents at 20 °C. Inset: The curves were fitted with one-order reaction dynamics ($\ln A = -kt$). [**2**] = 500 µmol/L, [Zn(II)] = 5 mmol/L, $\lambda = 494$ nm.



Figure S5. The thermal recovery kinetics of **3-Zn** in different solvents at 20 °C. Inset: The curves were fitted with one-order reaction dynamics ($\ln A = -kt$). [**3**] = 500 µmol/L, [Zn(II)] = 5 mmol/L, $\lambda = 585$ nm.



Figure S6. Stationary Born-Oppenheimer states of the complexes in different forms.

2. Caption of the video

Video 1. A video of letters recording on 1-Zn, 2-Zn and 3-Zn in silica gel. $[1] = [2] = [3] = 2 \mu \text{mol/g}$, $[\text{Zn}(\text{II})] = 200 \mu \text{mol/g}$, the wavelength of laser is 405 nm.

3. NMR spectra



Figure S7. ¹H-NMR spectra of 1.



Figure S8. ¹³C-NMR spectra of 1.



Figure S9. ¹H-NMR spectra of 2.



Figure S10. ¹³C-NMR spectra of 2.



Figure S11. ¹H-NMR spectra of 3.



Figure S12. ¹³C-NMR spectra of 3.



Figure S13. ¹H-NMR spectra of 4.



Figure S14. ¹³C-NMR spectra of 4.

4. ESI-MS



Figure S15. EMI-MS spectra of 1-Zn.



Figure S16. EMI-MS spectra of 2-Zn.



Figure S17. EMI-MS spectra of 3-Zn.



Figure S18. EMI-MS spectra of 1.



Figure S19. EMI-MS spectra of 2.



Figure S20. EMI-MS spectra of 3.



Figure S21. EMI-MS spectra of 4.