### **Electronic Supplementary Information**

# Three Rhodamine Based "off-on" Chemosensors with High Selectivity and Sensitivity for Fe<sup>3+</sup> Imaging in Living Cells

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### 1. Molecular structures of Y1 and Y2



FIGURE S1. Molecular structures of Y1 (a) and Y2 (b).

# 2. The fluorescence titration of Y1 (20 $\mu M)$ with $Fe^{3+}$



**FIGURE S2.** Fluorescence spectra changes of **Y1** (20  $\mu$ M) in methanol-water solution (4.5/5.5, v/v) upon addition of Fe<sup>3+</sup> (0-1.5 equiv),  $\lambda_{ex} = 550$  nm. Inset: Changes in the emission intensity at 580 nm.

# 3. UV-Vis titration of Y1 (20 $\mu$ M) with Fe<sup>3+</sup>



**FIGURE S3.** Changes in UV-Vis absorption spectra of **Y1** (20  $\mu$ M) in methanol-water solution (4.5/5.5, v/v) with various amounts of Fe<sup>3+</sup> (0-1.5 equiv). Inset: Job's plot of **Y3** and Fe<sup>3+</sup>.

### 4. Selective and competitive experiments of Y1



**FIGURE S4.** Fluorescence (a) and absorption (b) spectra of **Y1** (20  $\mu$ M) in methanol-water solution (4.5/5.5, v/v) upon addition of various metal ions (20  $\mu$ M),  $\lambda_{ex} = 550$  nm.



FIGURE S5. Fluorescence intensity (a) and absorption (b) changes of Y1 (20  $\mu$ M) upon the addition of various metal ions (20  $\mu$ M) in and without the presence of Fe<sup>3+</sup> (20  $\mu$ M) in methanol-water solution (4.5/5.5, v/v). Black bars represent the fluorescence response of Y1 to the metal ions of interest. 1: blank; 2: Li<sup>+</sup>; 3: Na<sup>+</sup>; 4: K<sup>+</sup>; 5: Ba<sup>2+</sup>; 6: Ca<sup>2+</sup>; 7: Cd<sup>2+</sup>; 8: Ag<sup>+</sup>; 9: Mg<sup>2+</sup>; 10: Co<sup>2+</sup>; 11: Mn<sup>2+</sup>; 12: Zn<sup>2+</sup>; 13: Pb<sup>2+</sup>; 14: Hg<sup>2+</sup>; 15: Ni<sup>2+</sup>; 16: Cr<sup>3+</sup>; 17: Cu<sup>2+</sup>; 18: Fe<sup>2+</sup>; 19: Fe<sup>3+</sup>. The chromatic bars represent the subsequent addition of 20  $\mu$ M Fe<sup>3+</sup> to the above solutions.

### 5. Ethylenediamine titration of Y1



**FIGURE S6.** Fluorescence intensity changes of **Y1** (20  $\mu$ M) upon the addition of each equiv of ethylenediamine with the presence of Fe<sup>3+</sup> (20  $\mu$ M) in methanol-water solution (4.5/5.5, v/v).

# 6. The fluorescence titration of Y2 (20 $\mu M$ ) with $Fe^{3+}$



**FIGURE S7.** Fluorescence spectra changes of **Y2** (20  $\mu$ M) in methanol-water solution (4.5/5.5, v/v) upon addition of Fe<sup>3+</sup> (0-1.5 equiv),  $\lambda_{ex} = 550$  nm. Inset: Changes in the emission intensity at 580 nm.

## 7. UV-Vis titration of Y2 (20 $\mu$ M) with Fe<sup>3+</sup>



**FIGURE S8.** Changes in UV-Vis absorption spectra of **Y2** (20  $\mu$ M) in methanol-water solution (4.5/5.5, v/v) with various amounts of Fe<sup>3+</sup> (0-1.5 equiv). Inset: Job's plot of **Y2** and Fe<sup>3+</sup>.

### 8. Selective and competitive experiments of Y2



**FIGURE S9.** Fluorescence (a) and absorption (b) spectra of **Y2** (20  $\mu$ M) in methanol-water solution (4.5/5.5, v/v) upon addition of various metal ions (20  $\mu$ M),  $\lambda_{ex} = 550$  nm.



**FIGURE S10.** Fluorescence intensity (a) and absorption (b) changes of **Y2** (20  $\mu$ M) upon the addition of various metal ions (20  $\mu$ M) in and without the presence of Fe<sup>3+</sup> (20  $\mu$ M) in methanol-water solution (4.5/5.5, v/v). Black bars represent the fluorescence response of **Y2** to the metal ions of interest. 1: blank; 2: Li<sup>+</sup>; 3: Na<sup>+</sup>; 4: K<sup>+</sup>; 5: Ba<sup>2+</sup>; 6: Ca<sup>2+</sup>; 7: Cd<sup>2+</sup>; 8: Ag<sup>+</sup>; 9: Mg<sup>2+</sup>; 10: Co<sup>2+</sup>; 11: Mn<sup>2+</sup>; 12: Zn<sup>2+</sup>; 13: Pb<sup>2+</sup>; 14: Hg<sup>2+</sup>; 15: Ni<sup>2+</sup>; 16: Cr<sup>3+</sup>; 17: Cu<sup>2+</sup>; 18: Fe<sup>2+</sup>; 19: Fe<sup>3+</sup>. The chromatic bars represent the subsequent addition of 20  $\mu$ M Fe<sup>3+</sup> to the above solutions.

### 9. Ethylenediamine titration of Y2



**FIGURE S11.** Fluorescence intensity changes of **Y2** (20  $\mu$ M) upon the addition of each equiv of ethylenediamine with the presence of Fe<sup>3+</sup> (20  $\mu$ M) in methanol-water solution (4.5/5.5, v/v).

### 10. Selective experiments of Y3



**FIGURE S12.** Fluorescence (a) and absorption (b) spectra of **Y3** (20  $\mu$ M) in methanol-water solution (4.5/5.5, v/v) upon addition of various metal ions (20  $\mu$ M),  $\lambda_{ex} = 550$  nm.



FIGURE S13. Absorption (a) and fluorescence intensity (b) changes of Y3 (20  $\mu$ M) upon the addition of various metal ions (20  $\mu$ M) in and without the presence of Fe<sup>3+</sup> (20  $\mu$ M) in methanol-water solution (4.5/5.5, v/v). Black bars represent the fluorescence response of Y3 to the metal ions of interest. 1: blank; 2: Li<sup>+</sup>; 3: Na<sup>+</sup>; 4: K<sup>+</sup>; 5: Ba<sup>2+</sup>; 6: Ca<sup>2+</sup>; 7: Cd<sup>2+</sup>; 8: Ag<sup>+</sup>; 9: Mg<sup>2+</sup>; 10: Co<sup>2+</sup>; 11: Mn<sup>2+</sup>; 12: Zn<sup>2+</sup>; 13: Pb<sup>2+</sup>; 14: Hg<sup>2+</sup>; 15: Ni<sup>2+</sup>; 16: Cr<sup>3+</sup>; 17: Cu<sup>2+</sup>; 18: Fe<sup>2+</sup>; 19: Fe<sup>3+</sup>. The chromatic bars represent the subsequent addition of 20  $\mu$ M Fe<sup>3+</sup> to the above solutions.

### 11. Ethylenediamine titration of Y3



**FIGURE S14.** Fluorescence intensity changes of **Y3** (20  $\mu$ M) upon the addition of each equiv of ethylenediamine with the presence of Fe<sup>3+</sup> (20  $\mu$ M) in methanol-water solution (4.5/5.5, v/v).

#### 12. Equations used for the calculation of association constant

The association constant was determined according to the references<sup>2</sup>. The probes bind with  $Fe^{3+}$  to form the complex in the 1:1 binding mode, the equilibrium can be described as follows:

$$R + Fe^{3+} \underbrace{K}_{[RFe]^{3+}} (12-1)$$

Here, R and  $[RFe]^{3+}$  denote the probe and the complex, respectively, and K denotes the association constant. The relative absorbance R is defined as the ratio of free R.  $[R]_f$  is defined as the total amount of R.  $[R]_t$  is defined as the absorbance in the methanol/water solution (4.5/5.5, v/v). It can be experimentally determined by measuring the absorbance values in the presence of different concentrations of Fe<sup>3+</sup>

$$\alpha = \frac{[R]_{f}}{[R]_{t}} = \frac{A_{t} - A}{A_{t} - A_{0}} \quad (12-2)$$

Here,  $A_0$  and  $A_t$  are the limiting absorbance values for  $\alpha=1$  (in the absence of Fe<sup>3+</sup>) and  $\alpha=0$  (the probe is completely complexed with Fe<sup>3+</sup>), respectively. The relationship between the probe and the Fe<sup>3+</sup> concentration can be represented as follows:

$$\frac{\alpha}{1-\alpha} = \frac{1}{\mathrm{K[Fe^{3+}]}} \quad (12-3)$$

It is apparent from Equation 12-4 that the relative absorbance  $\alpha$  has a distinct functional relationship with the concentration of Fe<sup>3+</sup> and the association constant K, which provides the basis for the detection of the K value. The experimental data were fitted to Equation 12-4 by adjusting the K value.

#### 13. Equations used for the calculation of fluorescence quantum yield

Fluorescence quantum yields ( $\Phi$ ) were determined using optically matching solutions of rhodamine B ( $\Phi_f = 0.97$  in ethanol) as standards at an excitation wavelength of 558 nm and the quantum yields were calculated using Equation 12-1 according to the references<sup>1</sup>. Where  $\Phi_u$  and  $\Phi_s$  are the fluorescence quantum yields of the sample and standard,  $I_u$  and  $I_s$  are the integrated emission intensities of the corrected spectra for the sample and standard,  $A_u$  and  $A_s$  are the absorbance of the sample and standard at the excitation wavelength (558 nm in all cases), and  $\eta_u$  and  $\eta_s$ are the indices of refraction of the sample and standard solutions, respectively.

$$\Phi u = \Phi s \cdot \frac{Iu}{Is} \cdot \frac{As}{Au} \cdot \left(\frac{\eta u}{\eta s}\right)^2 \quad (13-1)$$

#### 14. References

- (1) Huang, W.; Song, C. X.; He, C.; Lv, G. J.; Hu, X. Y.; Zhu, X.; Duan, C. Y. *Inorg. Chem.* **2009**, *48*, 5061-5072.
- (2) (a) Bourson, J.; Pouget, J.; Valeur, B. J. Phys. Chem. 1993, 97, 4552-4557. (b) Zhao, Y.; Zhang, X. B.; Han, Z. X.; Qiao, L.; Li, C. Y.; Jian, L. X.; Shen, G. L.; Yu, R. Q. Anal. Chem. 2009, 81, 7022-7030.

#### **15. Computation details**

#### 15.1. Computational methods

**Computational methods:** All the calculations were performed at B3LYP level with Gaussian 03 Program. Fe element was described with TZVP basis set, Cl element was described with  $6-311++G^{**}$  basis set, S, N and O elements were described with  $6-31++G^{*}$  basis set and  $6-31G^{**}$  basis set was used for C and H elements. Default type of grids in Guassian 03 Program for the numerical integration in DFT calculations was utilized. The computed total energies (Table S1) and Cartesian coordinates of the probe **Y3** (Table S2) and **Y3**-Fe<sup>3+</sup> complex (Table S3) were shown below.

#### 15.2. Geometry structures

**Geometry structures:** The geometry structures of the probe **Y3** and **Y3**-Fe<sup>3+</sup> complex were optimized (Figure S13). The optimized structures were confirmed to be local minima as shown by the fact that there was no imaginary frequency. It was clearly shown that Fe<sup>3+</sup> was mainly coordinated with N atom of benzothiazole moiety with the average distance of 1.922 Å, which was much shorter than the sum of the Van der Waals radii of Fe and N (3.35 Å). On the other hand, the distance between the carbonyl O atom and Fe was 5.409 Å, longer than the sum of the Van der Waals radii (3.34 Å), indicating that the O atom was hard to coordinate with Fe<sup>3+</sup>. The bond length of N4-C25 changed from 1.386 Å (**Y3**) to 1.358 Å (**Y3**-Fe<sup>3+</sup>), while the length of C16-C28 changed from 1.516 Å (**Y3**) to 1.408 Å (**Y3**-Fe<sup>3+</sup>), indicating the existence of the quinoid structure in **Y3**-Fe<sup>3+</sup> (Figure S13). This fact showed the ring-opening progress in **Y3** upon coordinated with Fe<sup>3+</sup>.

#### 15.3. NBO analysis

**NBO analysis:** The priority of the N atom over the O atom in coordination with  $Fe^{3+}$  may be explained based on the NBO analysis of the lone pair (LP) orbitals of N and O atoms. The LP of the N atom was  $sp^{2.42}$  hybridization (70.67% in contribution from p orbital), while the hybridization of the LP of the O atom was  $sp^{0.72}$  (41.71% contribution from p orbital). The larger amount of the contribution of p orbital would lead to a higher degree of diffuseness of the LP orbital. Therefore, the spatial extent of the LP of N atom would be larger than that of O atom, and thus facilitates its contact with Fe<sup>3+</sup>. In energetic terms, the orbital energy of the LP of the N atom was -212.45 kcal/mol, significantly higher than that of O atom (-423.57 kcal/mol). Therefore, compared with O atom, the coordination of the Fe<sup>3+</sup> to the N atom should be more energetically favorable.



**FIGURE S15.** B3LYP optimized structure of **Y3** (a) and **Y3-**Fe<sup>3+</sup> (b) complex. Carbon atoms are gray, oxygen atoms are red, nitrogen atoms are blue, sulfur atoms are yellow, chlorine atoms are green, and iron atom is steelblue.

**TABLE S1.** Computed total energies of **Y3** and **Y3**-Fe<sup>3+</sup> complex.

Compound	Total energy (a.u.)
Y3	-2236.4460925
<b>Y3-</b> Fe <sup>3+</sup> complex	-4880.98793

	Co	oordinates (Angstron	ns)
Atom	X	Y	Z
S	-1.5293	1.37532	3.1015
Ν	-0.21237	1.21207	0.82569
Ν	-1.11502	-0.85078	1.50735
Ν	5.19455	-1.48729	0.18159
Ν	-2.82932	0.49635	-4.56299
0	-0.0689	6.43464	2.69613
Ο	-2.36207	-1.23362	3.43318
0	0.9982	-0.49979	-1.90084
С	-0.70675	6.79127	3.91408
Н	-0.52857	7.85922	4.0448
Н	-0.28009	6.24497	4.76483
Н	-1.78751	6.60608	3.87001
С	-0.13902	5.12669	2.28547
С	0.51724	4.84516	1.06847
Н	1.01705	5.66176	0.55834

TABLE S2. Cartesian coordinates of the probe Y3

С	0.52104	3.56399	0.54404
Н	1.0241	3.34204	-0.3914
С	-0.13799	2.53386	1.23532
С	-0.78963	2.83045	2.44998
С	-0.80126	4.12117	2.99212
Н	-1.3088	4.32257	3.92733
С	-0.88973	0.50376	1.67483
С	-1.83951	-1.63858	2.40002
С	-1.83427	-3.00662	1.84587
С	-2.42102	-4.16029	2.36671
Н	-2.97177	-4.12091	3.30113
С	-2.27136	-5.34498	1.64794
Н	-2.7128	-6.26461	2.02009
С	-1.5517	-5.35996	0.44251
Н	-1.44587	-6.29347	-0.10285
С	-0.96922	-4.19752	-0.06875
Н	-0.4141	-4.21533	-1.00159
С	-1.12039	-3.016	0.65106
С	-0.58736	-1.62548	0.30893
С	0.92853	-1.59729	0.26693
С	1.70501	-2.10395	1.32026
Н	1.20351	-2.55253	2.17349
С	3.08775	-2.05581	1.31444
Н	3.62255	-2.48077	2.15398
С	3.79049	-1.49095	0.2184
С	3.01843	-0.97526	-0.83594
Н	3.46264	-0.49143	-1.69455
С	1.62275	-1.03773	-0.80398
С	-0.37105	-0.55123	-1.98895
С	-0.90123	-0.03482	-3.17003
Н	-0.19759	0.34354	-3.89916
С	-2.29128	-0.02699	-3.39738
С	-3.11409	-0.58298	-2.38196
Н	-4.19105	-0.59458	-2.48626
С	-2.55517	-1.10106	-1.22552
Н	-3.2183	-1.51179	-0.4689
С	-1.17409	-1.09821	-0.986
С	5.91565	-1.3103	1.44998
Н	6.95439	-1.60545	1.28839
Н	5.52622	-2.0228	2.17928
С	5.85352	0.11155	2.02486
Н	6.40911	0.16651	2.96716
Н	4.81921	0.40932	2.22142
Н	6.29087	0.84177	1.33588

С	5.83317	-0.92893	-1.01555
Н	5.68333	0.16259	-1.08533
Н	5.32709	-1.36777	-1.88001
С	7.3243	-1.24438	-1.1408
Н	7.66733	-0.93951	-2.13438
Н	7.51143	-2.31748	-1.03255
Н	7.93745	-0.70951	-0.41005
С	-4.25829	0.41749	-4.85346
Н	-4.64458	-0.54831	-4.51249
Н	-4.37126	0.41283	-5.94355
С	-5.0837	1.56535	-4.25594
Н	-6.14098	1.45931	-4.52288
Н	-4.73554	2.53295	-4.63197
Н	-5.00424	1.58274	-3.16536
С	-2.00532	1.22113	-5.52648
Н	-1.23705	1.78815	-4.99055
Н	-2.64339	1.96938	-6.0103
С	-1.36316	0.32733	-6.59575
Н	-0.76886	0.92805	-7.29315
Н	-2.12843	-0.20216	-7.17294
Н	-0.7073	-0.42194	-6.14357

**TABLE S3.** Cartesian coordinates of the **Y3**-Fe<sup>3+</sup> complex

	Coordinates (Angstroms)		
Atom	Х	Y	Z
Fe	4.08439	1.56113	0.37523
Cl	4.50501	0.0585	1.94654
Cl	5.33196	2.90411	-0.79266
Cl	2.70345	2.82208	1.46082
S	1.57524	-0.86901	-2.44014
Ν	3.29749	0.45548	-0.98541
Ν	1.21895	1.53083	-1.09107
Ν	-7.35416	-1.30238	-1.39681
Ν	0.54217	-1.93916	3.84498
Ο	5.76785	-3.9503	-3.31795
Ο	-0.70773	0.49748	-1.89557
Ο	-3.39608	-1.34333	1.24613
С	5.03051	-4.81827	-4.16525
Н	4.19999	-5.29409	-3.6279
Н	5.73288	-5.58479	-4.49478
Н	4.63706	-4.28598	-5.04069

С	5.11464	-2.87759	-2.76393
С	3.76474	-2.59029	-2.97078
Н	3.13818	-3.20842	-3.60218
С	3.23017	-1.45967	-2.34361
С	4.00519	-0.6295	-1.52107
С	5.36492	-0.92547	-1.33478
Н	5.99527	-0.29222	-0.72117
С	5.90529	-2.0429	-1.95134
Н	6.95314	-2.29152	-1.82392
С	2.02116	0.52888	-1.40765
С	-0.10123	1.45014	-1.36423
С	-0.88402	2.65825	-0.91593
С	-0.44314	3.94789	-1.22819
Н	0.50696	4.0598	-1.73942
С	-1.20472	5.0642	-0.8826
Н	-0.85261	6.05865	-1.13982
С	-2.4111	4.90201	-0.1995
Н	-3.00331	5.76744	0.08255
С	-2.84868	3.6228	0.1426
Н	-3.76512	3.49716	0.71231
С	-2.09274	2.49293	-0.20769
С	-2.52793	1.15307	0.26662
С	-3.75733	0.58712	-0.16506
С	-4.61993	1.17299	-1.12926
Н	-4.33051	2.11816	-1.57278
С	-5.79253	0.57552	-1.51692
Н	-6.40498	1.07805	-2.25282
С	-6.19879	-0.69084	-0.98106
С	-5.34673	-1.29221	-0.02674
Н	-5.57263	-2.24523	0.42977
С	-4.1661	-0.67151	0.34552
С	-2.19809	-0.83598	1.66041
С	-1.47195	-1.62282	2.52953
Н	-1.8825	-2.58643	2.7966
С	-0.20936	-1.17983	3.00641
С	0.24385	0.11573	2.57781
Н	1.19267	0.51007	2.91554
С	-0.50036	0.88373	1.72797
Н	-0.10859	1.84927	1.43419
С	-1.75221	0.43862	1.20055
С	-8.25519	-0.66043	-2.36336
Н	-7.66038	-0.23	-3.17488
Н	-8.8499	-1.45615	-2.81995
С	-9.1866	0.40052	-1.76337

Н	-9.86175	-0.03747	-1.02287
Н	-9.79699	0.85147	-2.55264
Н	-8.6208	1.19799	-1.2737
С	-7.76923	-2.59308	-0.83368
Н	-8.44354	-3.0568	-1.55869
Н	-6.89491	-3.24977	-0.77436
С	-8.46264	-2.50391	0.53216
Н	-7.82383	-2.01908	1.2755
Н	-8.70414	-3.50859	0.89432
Н	-9.39474	-1.93572	0.46654
С	0.06748	-3.22972	4.3575
Н	-1.00357	-3.16318	4.56913
Н	0.55684	-3.38799	5.32317
С	0.36853	-4.40396	3.41883
Н	-0.1198	-4.27322	2.44912
Н	0.01392	-5.3409	3.86047
Н	1.44432	-4.49683	3.24266
С	1.90392	-1.54807	4.25704
Н	2.46224	-2.47628	4.41292
Н	2.4056	-1.03388	3.43576
С	1.9294	-0.69934	5.53099
Н	1.39571	0.24479	5.38921
Н	2.9646	-0.46501	5.79636
Н	1.47105	-1.22733	6.37415

16. IR, <sup>1</sup>HNMR and <sup>13</sup>C NMR spectra of Y1-Y3 and Y3-Fe<sup>3+</sup>.



**FIGURE S16.** IR spectra of compound **Y3** (a) and **Y3**-Fe<sup>3+</sup> complex (b) in KBr disks.



FIGURE S17. IR spectrum of Y1 in KBr disks.



FIGURE S18. IR spectrum of Y2 in KBr disks.



FIGURE S19. IR spectrum of Y3 in KBr disks.



**FIGURE S20.** IR spectrum of **Y3**-Fe<sup>3+</sup> in KBr disks.



FIGURE S21. <sup>1</sup>H NMR spectrum of Y1 in CDCl<sub>3</sub>.



FIGURE S22. <sup>13</sup>C NMR spectrum of Y1 in CDCl<sub>3</sub>.



FIGURE S23. <sup>1</sup>H NMR spectrum of Y2 in CDCl<sub>3</sub>.



FIGURE S24. <sup>13</sup>C NMR spectrum of Y2 in CDCl<sub>3</sub>.



FIGURE S25. <sup>1</sup>H NMR spectrum of Y3 in CDCl<sub>3</sub>.



FIGURE S26. <sup>13</sup>C NMR spectrum of Y3 in CDCl<sub>3</sub>.