

## Supporting Information

### **A new rhodamine based chemodosimeter for Ni<sup>2+</sup> with high sensitivity and selectivity**

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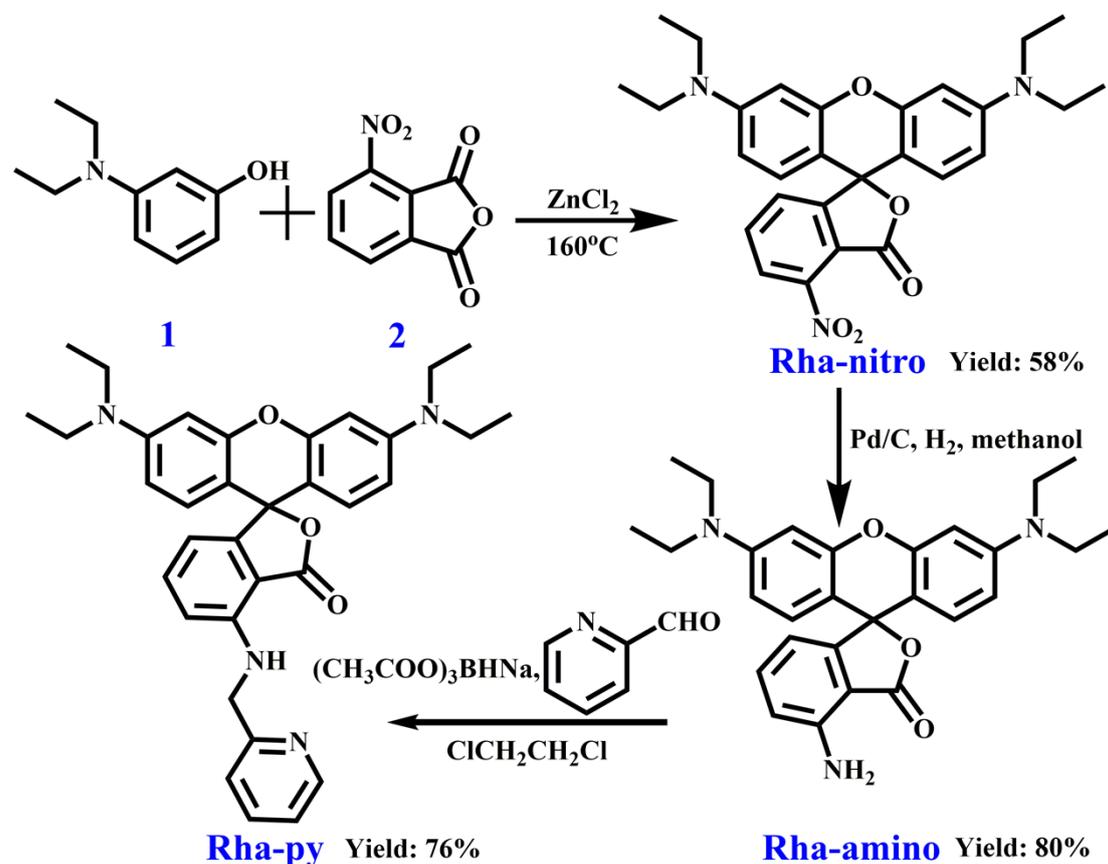
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## 1. Reagents and Apparatus

All chemicals were obtained from commercial suppliers and used without further purification. Spectroscopic grade solvents have been used for spectroscopic experiments. The solutions of metal ions were prepared from their nitrate salts, except for FeCl<sub>2</sub>, CoCl<sub>2</sub>, HgCl<sub>2</sub> and MnCl<sub>2</sub>. Water was purified by Milli-Q system. Other chemicals are of analytical reagent grade and used without further purification. Absorption spectra were measured on an Analytik Jena Specord®210 plus UV/VIS spectrophotometer, path length was 1 cm. All fluorescence measurements were carried out on a Shimadzu-RF5301 fluorescence spectrometer with both excitation and emission bandwidths set at 3.0 nm. All pH values were measured with Sartorius PB-21. <sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C NMR (126 MHz) spectra were recorded on a Bruker AVANCE500 using TMS as a standard at room temperature. All chemical shifts are reported in the standard notation of parts per million. LC-HRMS analysis was performed on an Agilent 1290-microTOF-Q II mass spectrometer. MALDI-TOF was obtained by Bruker Autoflex speed TOF/ TOF. IR spectra studies were performed on Vertex 80/80V FT-IR spectrometer with LN-MCT Mid DC detector over the range of 4000-800 cm<sup>-1</sup> using a KBr plate. Single-crystal X-ray diffraction data for **Rha-amino** was recorded on a Rigaku RAXIS-PRID diffractometer using the  $\omega$ -scan mode with graphite-monochromator Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Melting point was determined using a SGW X-4B microscopy melting point apparatus (Shanghai).

## 2. Synthesis of Rha-py



**Synthesis of Rha-nitro:** Synthesis of 3', 6'-bis (diethylamino)-4-nitro-3H-spiro [isobenzofuran-1,9'-xanthen]-3-one (**Rha-nitro**): Rha-nitro was synthesized via a similar route as Nagano's with slightly modification.<sup>1</sup> A mixture of 3-nitrophthalic anhydride (1.93 g, 10 mmol), zinc chloride (1.35g, 10 mmol) and N, N-diethyl-3-aminophenol (1.65 g, 10 mmol) was stirred at 110°C for 0.5h. Then added another part of zinc chloride (1.35 g, 10 mmol) and N, N-diethyl-3-aminophenol (1.65 g, 10 mmol), and stirred for 6 h at 160°C. The reaction was quenched by water. The petunia amorphous solid was refluxed in 2M HCl (100 mL) for 2 h. The mixture was neutralized with sodium hydroxide, and the violet precipitate was collected and dried. Extraction with dichloromethane could also be used for collection. The products were purified by chromatography (silica, 10% CH<sub>3</sub>OH in CH<sub>2</sub>Cl<sub>2</sub>) to afford the violet Rha-nitro (2.83 g, 58% yield); Melt point: 158-159°C. LC-HRMS: m/z calculated for [M + H]<sup>+</sup> 488.2180, found 488.2186. <sup>1</sup>H NMR: δ<sub>H</sub> (500 MHz, DMSO) 8.11 (1 H, d, *J*= 7.8), 7.86 (1 H, t, *J*=7.8), 7.57 (1 H, d, *J*= 7.7), 6.74 (2 H, d, *J*= 9.0), 6.68 – 6.56 (4 H, m), 3.44 (8 H, q, *J*= 6.6), 1.13 (12 H, t, *J*= 7.0). <sup>13</sup>C NMR: δ<sub>C</sub> (126 MHz, DMSO) 163.62, 153.85, 152.30, 150.85, 149.19, 146.43, 134.22, 129.62, 127.25, 124.32, 123.79, 109.85, 106.31, 96.59, 44.19, 12.33.

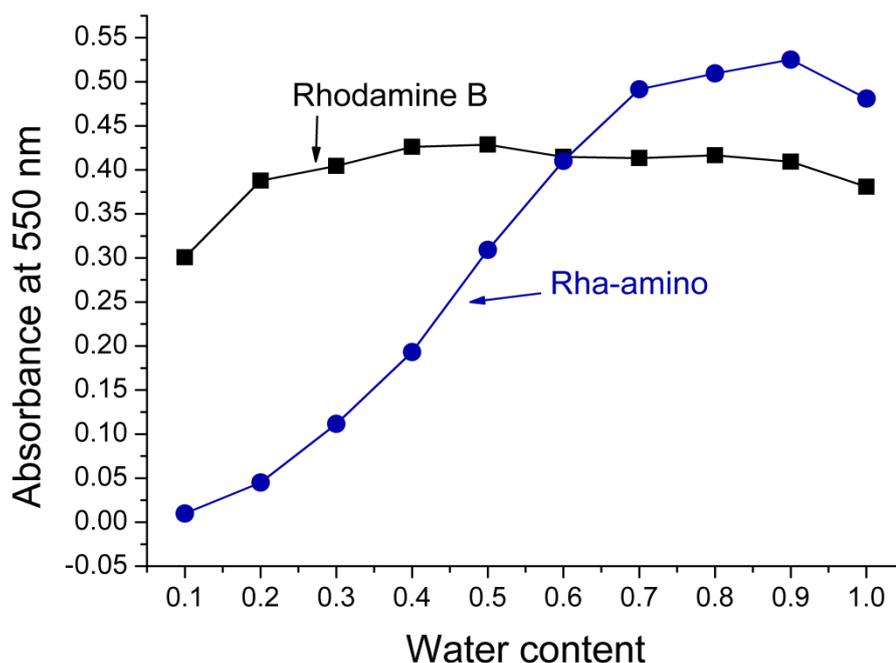
**Synthesis of Rha-amino:** Synthesis of 4-amino-3', 6'-bis (diethylamino)-3H-spiro [isobenzofuran-1,9'-xanthen]-3-one (**Rha-amino**): Rha-nitro (2.44g, 5.0 mmol) was reduced with 0.1g 10% Pd/C under hydrogen atmosphere to give Rha-amino.<sup>2</sup> The residue was filtered, the solution was evaporated and purified by chromatography (silica, 5% CH<sub>3</sub>OH in CH<sub>2</sub>Cl<sub>2</sub>) to give purple powder (1.84g, 80%). Melt point: 229-230°C. LC-HRMS: m/z calculated for [M + H]<sup>+</sup> 458.2438, found 458.2427. <sup>1</sup>H NMR: δ<sub>H</sub> (500 MHz, CDCl<sub>3</sub>) 7.34 (1 H, t, *J*=7.7), 6.69 (3 H, dd, *J*=21.6, 8.4), 6.42 (3 H, d, *J*= 7.4), 6.36 (2 H, d, *J*=8.1), 5.38 (2 H, s), 3.36 (8 H, q, *J*=7.0), 1.17 (12 H, t, *J*=7.0). <sup>13</sup>C NMR: δ<sub>C</sub> (126 MHz, DMSO) 170.14, 153.57, 152.41, 148.89, 147.44, 136.20, 128.57, 113.72, 109.73, 108.19, 108.05, 106.14, 96.88, 83.62, 43.77, 12.33.

**Synthesis of Rha-py:** Synthesis of 3', 6'-bis (diethylamino)-4-((pyridin-2-ylmethyl) amino) -3H-spiro [isobenzofuran -1, 9'-xanthen]-3-one (**Rha-py**). Rha-amino (0.487g, 1.0mmol), Sodium triacetoborohydride (0.424g, 2.0mmol) and 2-pyridinecarboxaldehyde (0.214g, 2.0mmol) was mixed in ClCH<sub>2</sub>CH<sub>2</sub>Cl with acetic acid catalysis under room temperature for 10h. The reaction was quenched by sodium hydrogen carbonate solution. Extraction with dichloromethane was used for collection. The product was purified by chromatography (silica, 3% CH<sub>3</sub>OH in CH<sub>2</sub>Cl<sub>2</sub>) to give the final product Rha-py (0.42g, 76%); Melt point: 160-161°C. LC-HRMS: m/z calculated for [M + H]<sup>+</sup> 549.2860, found 549.2851. <sup>1</sup>H NMR: δ<sub>H</sub> (300 MHz, DMSO) 8.61 (1 H, d, *J*= 4.4), 7.83 (1 H, td, *J*= 7.7, 1.7), 7.56 (1 H, t, *J*= 5.5), 7.50 - 7.38 (2 H, m), 7.37 - 7.26 (1 H, m), 6.69 (1 H, d, *J*= 8.3), 6.57 (2 H, d, *J*= 8.6), 6.50–6.35 (4 H, m), 6.25 (1 H, d, *J*= 7.3), 4.66 (2 H, d, *J*= 5.5), 3.35 (8 H, dd, *J*= 12.4, 5.3), 1.09 (12 H, t, *J*= 6.9). <sup>13</sup>C NMR: δ<sub>C</sub> (126 MHz, DMSO) 170.72, 158.09, 154.49, 152.90, 149.52, 149.45, 146.98, 137.42, 129.06, 122.89, 122.07, 120.00, 110.39, 110.27, 109.24, 108.59, 106.28, 97.38, 84.30, 47.77, 44.25, 12.82.

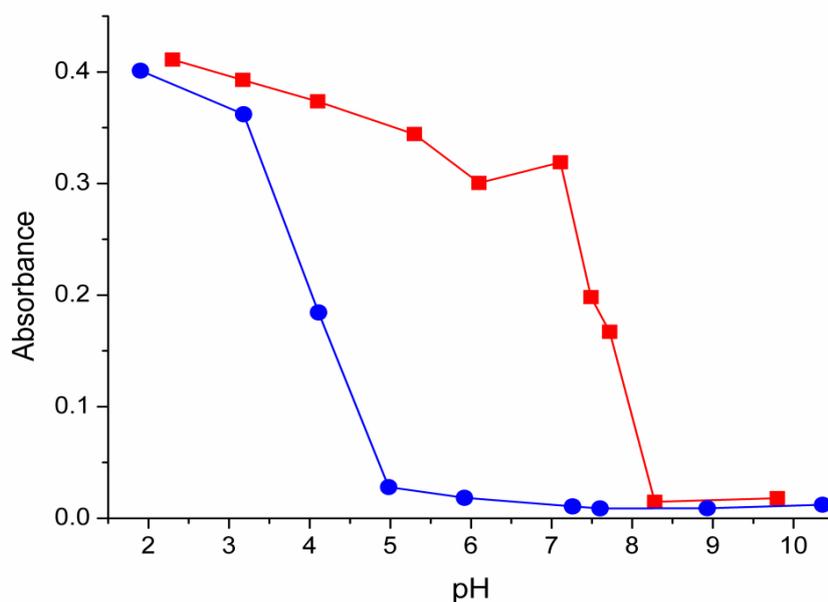
### 3. Spectroscopic Materials and Methods

Experiments involving the measurement of Rha-py absorbance and fluorescence were performed on CH<sub>3</sub>CN buffered with HEPES (9/1, v/v, pH=7.1, 20 mM). Stock solution of Rha-py ( $1 \times 10^{-4}$  M) was prepared in CH<sub>3</sub>CN. The UV-Vis absorption spectra were recorded from 200 nm to 800 nm. The fluorescence emission spectra were recorded at an excitation wavelength of 540 nm with emission wavelength ranging from 550 nm to 800 nm.

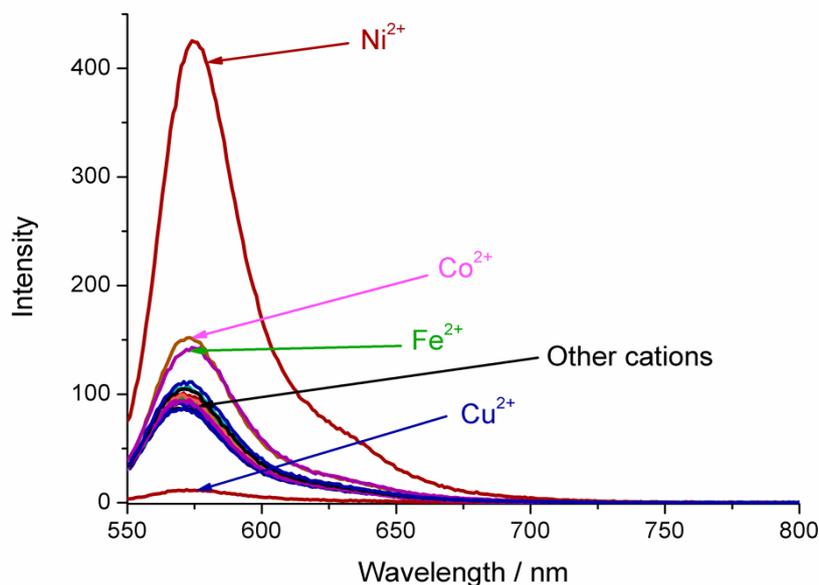
### 4. Optimization of experimental conditions



**Figure S1.** Plot of absorbance at 550 nm vs. water content in CH<sub>3</sub>CN. Black line and square dot represent the Rhodamine B (4  $\mu$ M). Blue line and circle dot represent Rha-amino (4  $\mu$ M). Contrast to Rhodamine B, the absorbance of Rha-amino increase along with water content, Rhodamine B exist major in its zwitterionic form through the process.

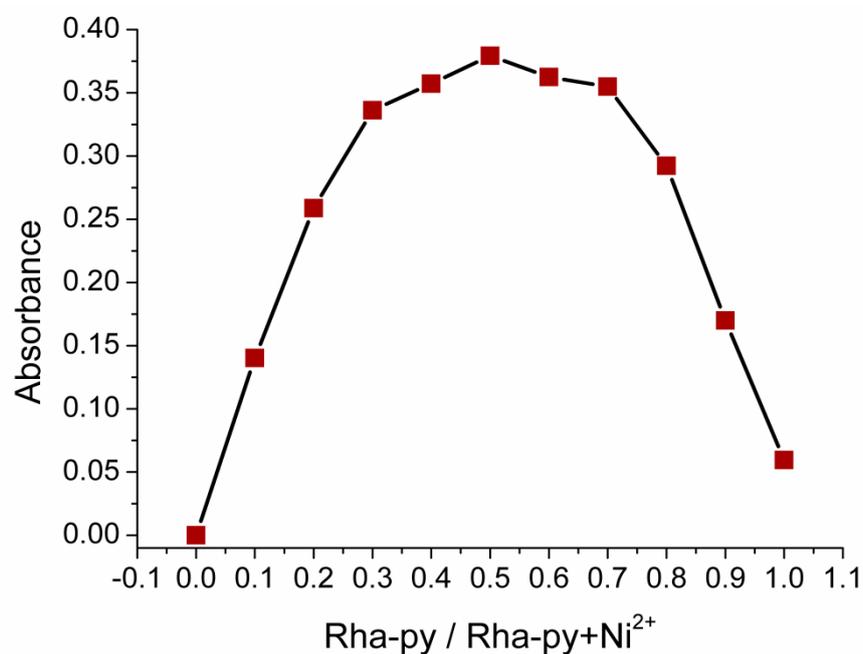


**Figure S2.** Absorbance of Rha-py (4  $\mu\text{M}$ ) in  $\text{CH}_3\text{CN}$  buffered with HEPES (9/1, v/v, pH=7.1, 20 mM) of different pH in the absence (bottom line, circle, at 550 nm) and presence (top line, square, at 550 nm) of 40  $\mu\text{M}$   $\text{Ni}^{2+}$ . The pH values were adjusted by aqueous solution of NaOH (aq, 1M) or HCl (aq, 1M). From the figure, the range between pH=4.5 to pH=7.5 is suitable for the detection of  $\text{Ni}^{2+}$  by colorimetric method. We chose pH=7.1 as the experiment condition.

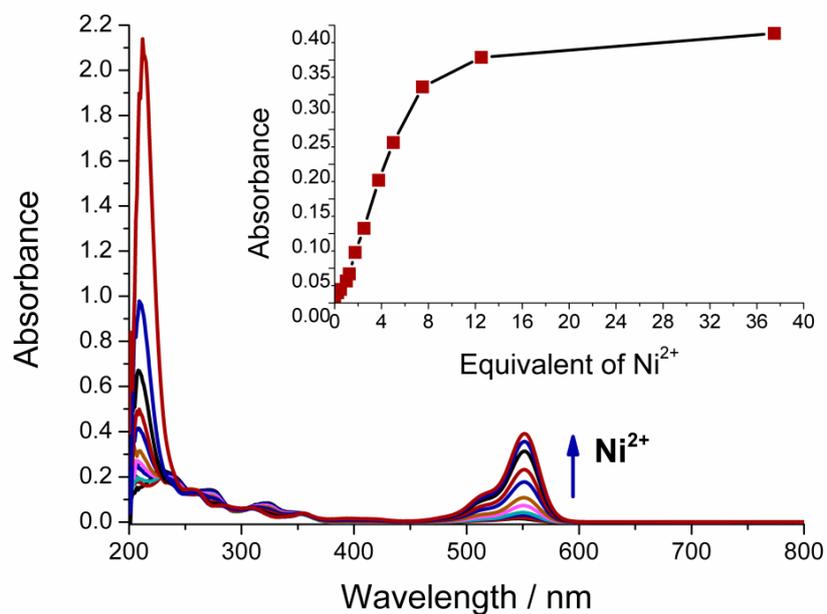


**Figure S3.** Fluorescence spectra of Rha-py (4  $\mu\text{M}$ ) in  $\text{CH}_3\text{CN}$  buffered with HEPES (9/1, v/v, pH=7.1, 20 mM) after the addition of different metal ions (40  $\mu\text{M}$ ). Metal ions:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ . Excitation was performed at 540 nm.

## 5. Determination of Ni<sup>2+</sup>



**Figure S4.** Job's plot of Rha-py and Ni<sup>2+</sup> with a total concentration of 20  $\mu\text{M}$  in CH<sub>3</sub>CN buffered with HEPES (9/1, v/v, pH=7.1, 20 mM), when the molar fraction of Ni<sup>2+</sup> was 0.5, the absorbance at 550 nm reached a maximum, indicating a 1:1 metal-ligand ratio.

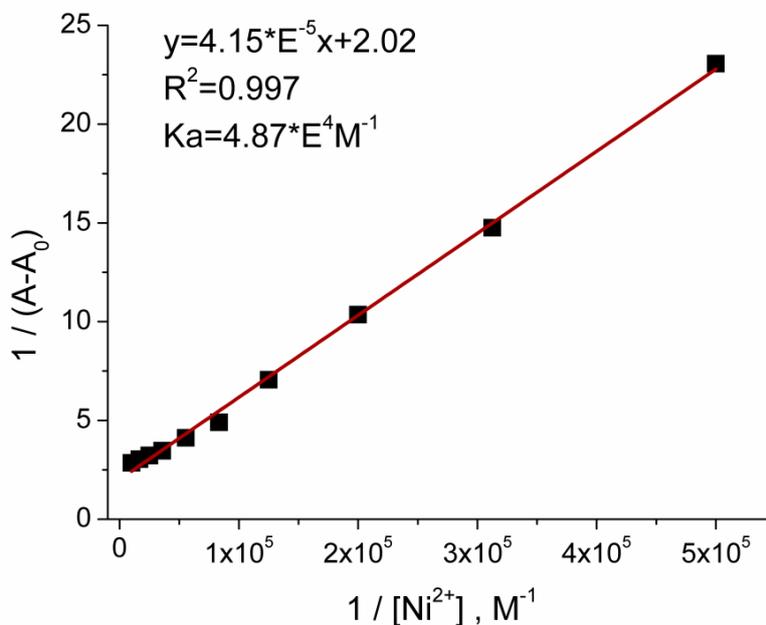


**Figure S5.** UV-Vis spectra of Rha-py (4  $\mu\text{M}$ ) upon the addition of Ni<sup>2+</sup>. Inset: plot of absorbance at 550 nm vs. number of equivalents of Ni<sup>2+</sup>.

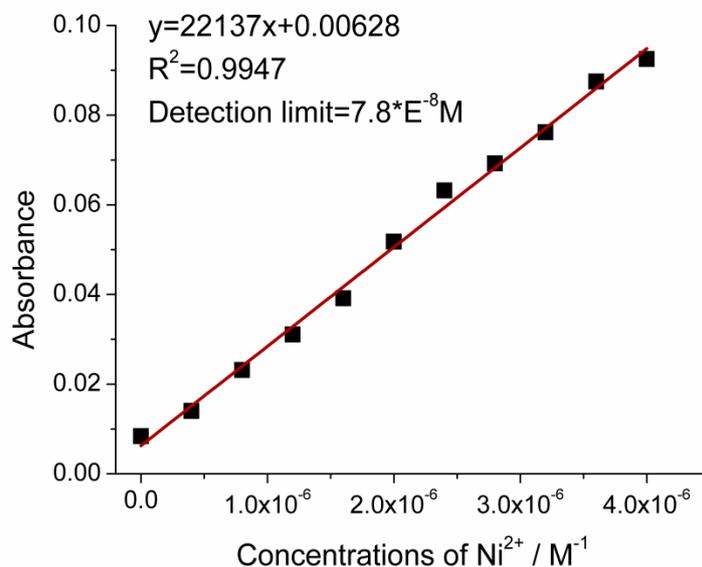
The association constant ( $K_a$ ) of Rha-py with  $\text{Ni}^{2+}$  was determined based on the absorbance titration curve using the Benesi-Hildebrand equation as follows<sup>3</sup>:

$$1/(A_{\max} - A_0) = [1/(A - A_0)] \times [1/(K_a \times [\text{Ni}^{2+}] + 1)]$$

where  $A$  and  $A_0$  represent the absorbance of host in the presence and absence of ions, respectively,  $A_{\max}$  is the saturated absorbance of host in the presence of excess amount of ions;  $[\text{Ni}^{2+}]$  is the concentration of  $\text{Ni}^{2+}$  added.



**Figure S6.** Benesi-Hildebrand plot of Rha-py with  $\text{Ni}^{2+}$ . From the plot, we can get the association constants ( $K_a$ ) of Rha-py and  $\text{Ni}^{2+}$  is  $4.87 \times 10^4 \text{ M}^{-1}$ .

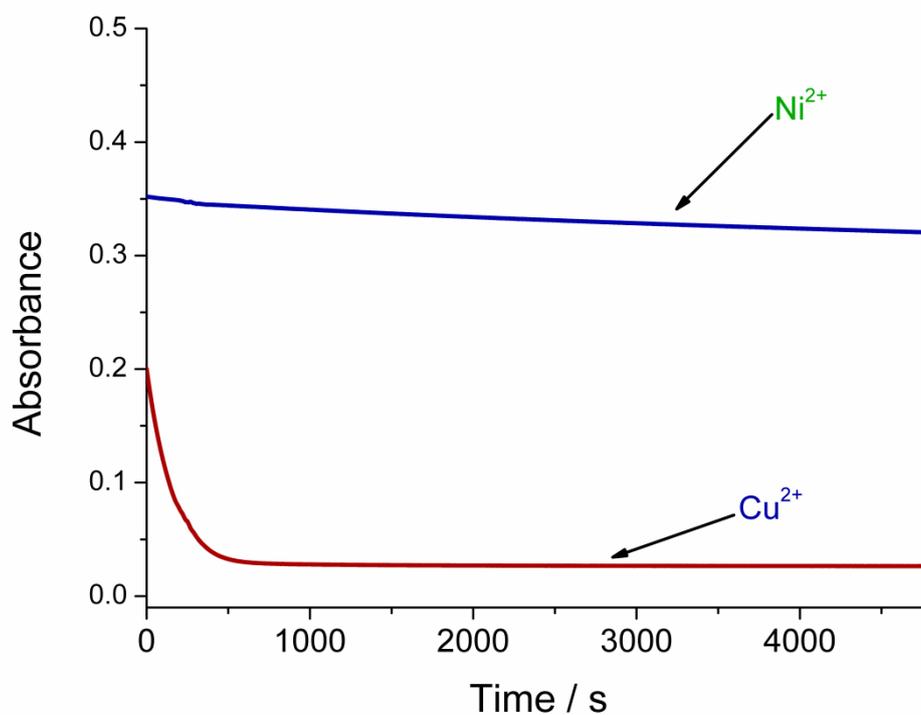


**Figure S7.** Plot of the absorbance at 550 nm for a mixture of Rha-py ( $4 \mu\text{M}$ ) in  $\text{CH}_3\text{CN}$  buffered with HEPES (9/1, v/v,  $\text{pH}=7.1$ ,  $20 \text{ mM}$ ). The detection limit for  $\text{Ni}^{2+}$  is  $7.8 \times 10^{-8} \text{ M}$ .

**Table S1.** Condition: Rha-py (4 $\mu$ M) in CH<sub>3</sub>CN buffered with HEPES (9/1, v/v, pH=7.1, 20 mM). The water sample was acquired at South Lake, Changchun and simply filtrated.

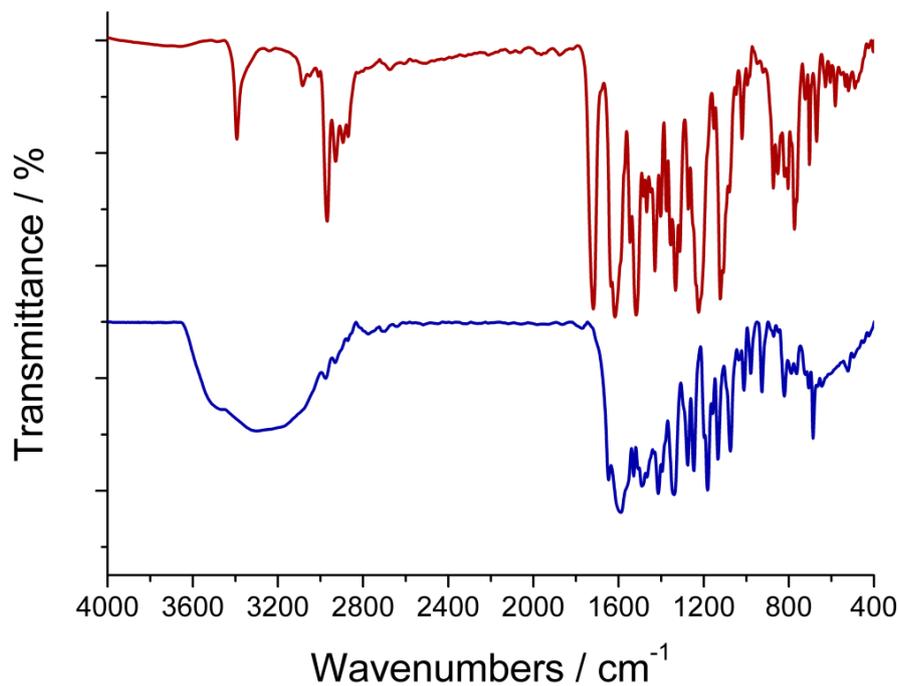
| Sample     | Ni <sup>2+</sup> added ( $\mu$ M) | Ni <sup>2+</sup> found ( $\mu$ M) | Recovery (%) | R.S.D. (%) |
|------------|-----------------------------------|-----------------------------------|--------------|------------|
| South Lake | 2.00                              | 1.89                              | 94.5         | 3.7        |
|            | 4.00                              | 3.84                              | 96.0         | 3.2        |

## 6. Discrimination of Cu<sup>2+</sup>

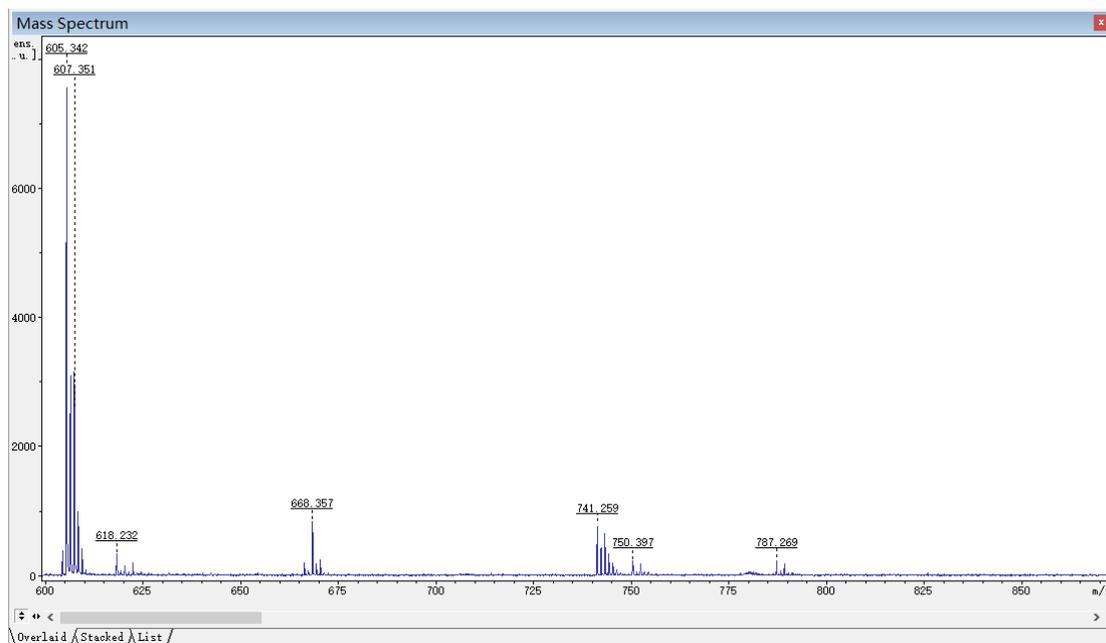


**Figure S8.** The blue line represented the change in absorption at 550 nm of Rha-py (4  $\mu$ M) in CH<sub>3</sub>CN buffered with HEPES (9/1, v/v, pH=7.1, 20 mM) with time in the presence of Ni<sup>2+</sup> (40 $\mu$ M). The red line represented the change in absorption at 540nm of Rha-py (4  $\mu$ M) and Cu<sup>2+</sup> (40 $\mu$ M) with time in the same buffer.

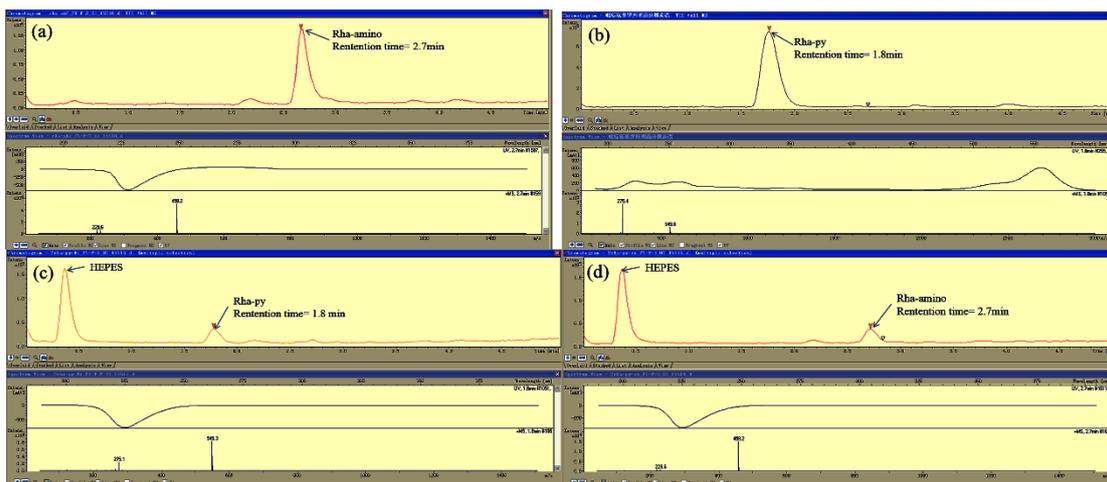
## 7. IR spectra, Mass spectroscopy, $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and X-Ray crystallographic analyses for Rha-amino



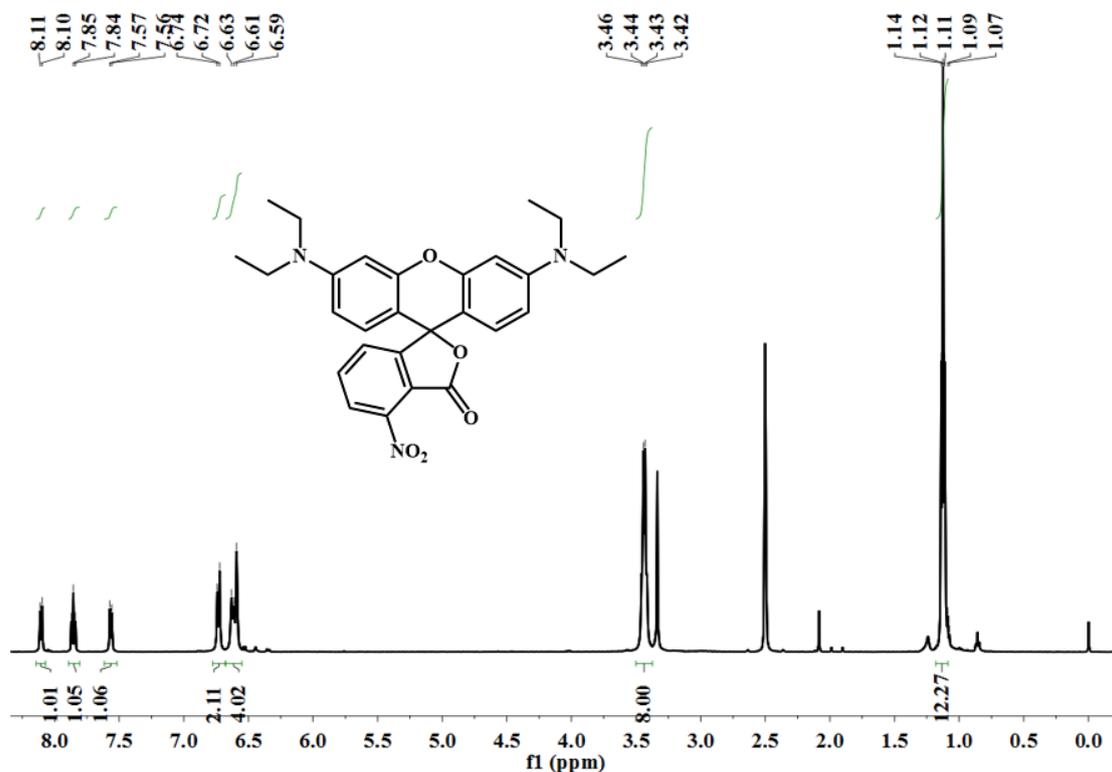
**Figure S9.** IR spectra of Rha-py and Rha-py- $\text{Ni}^{2+}$  in KBr, red line represented the infrared light absorbance of Rha-py, the blue line represented the infrared light absorbance of Rha-py- $\text{Ni}^{2+}$  in KBr disks.

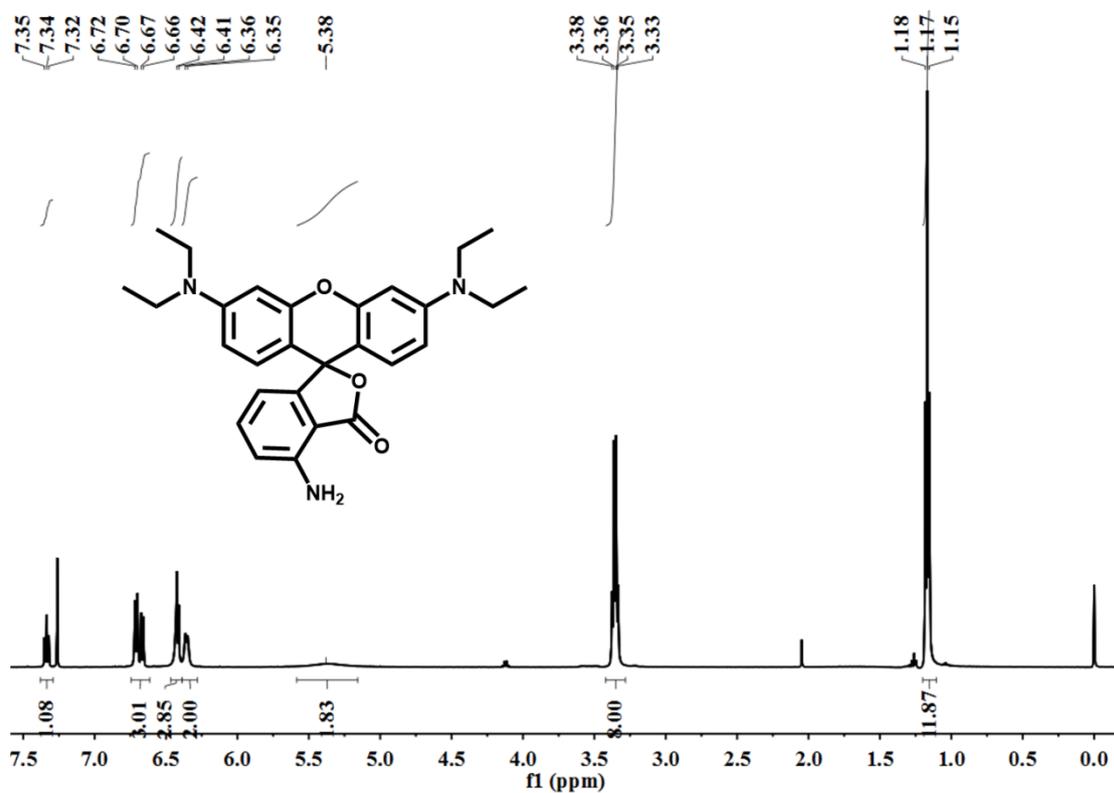
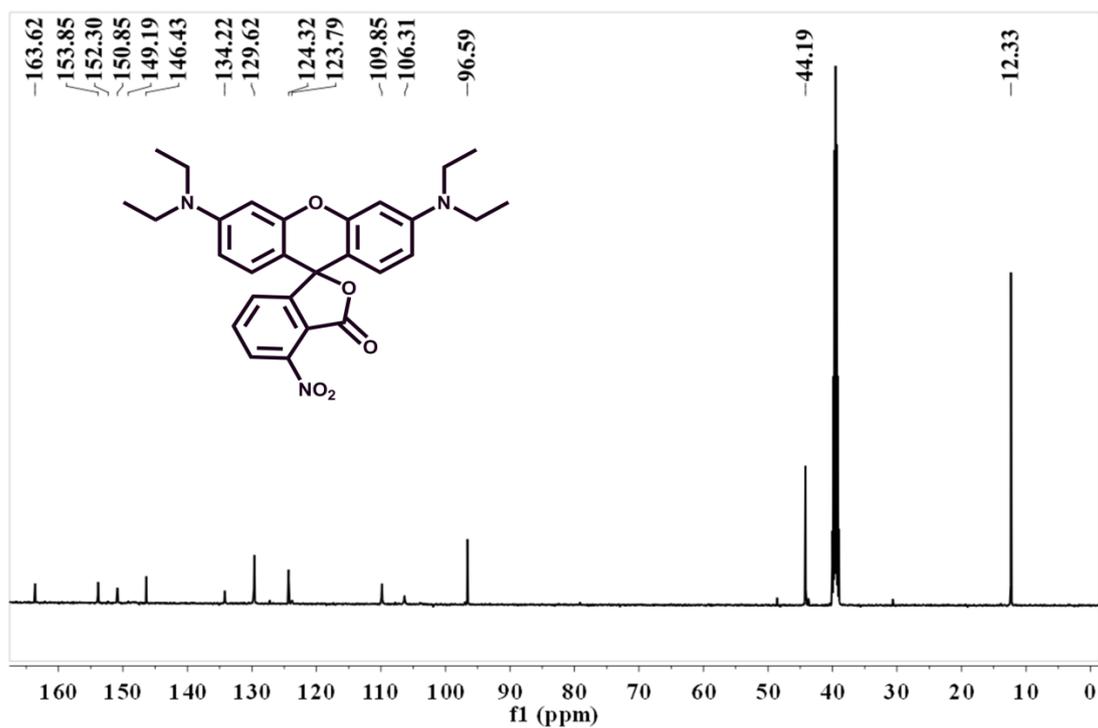


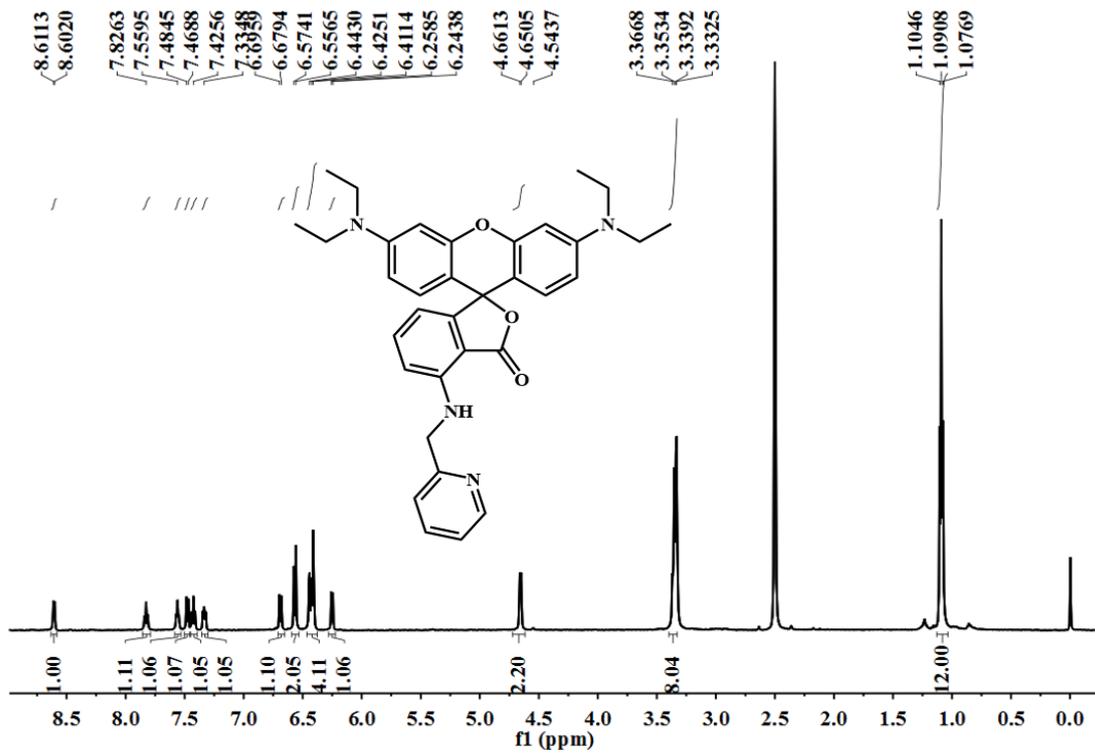
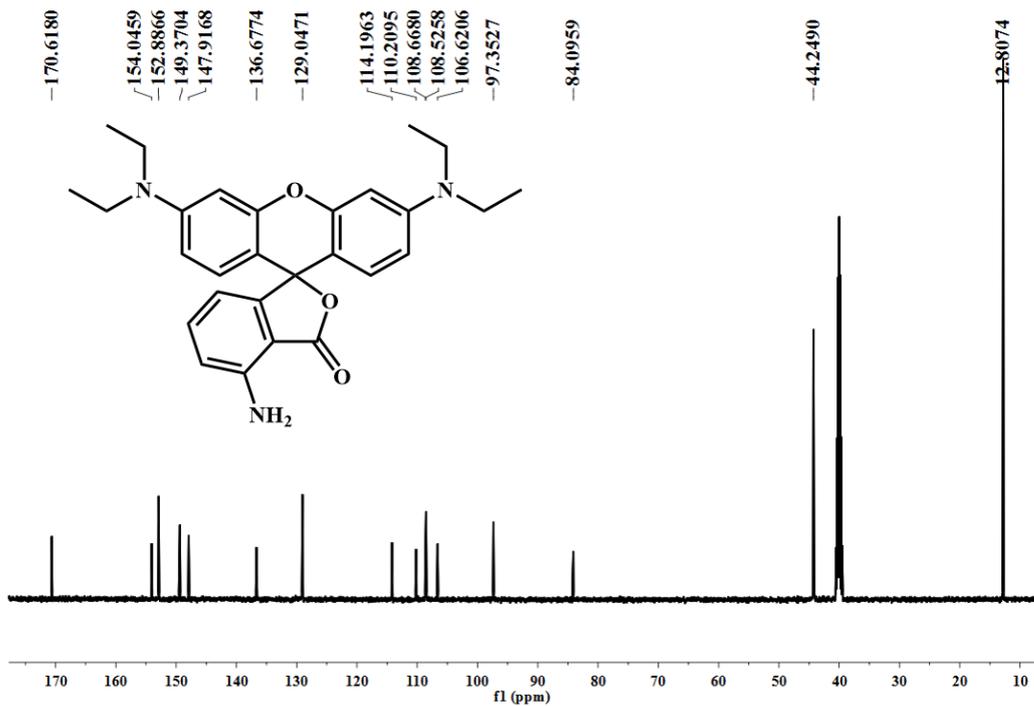
**Figure S10.** MALDI-TOF spectra of Rha-py and  $\text{Ni}^{2+}$ . The number 605.34 stood for the compound of  $\text{Ni}^{2+}$  and Rha-py, which confirmed the coordination ratio was 1:1.

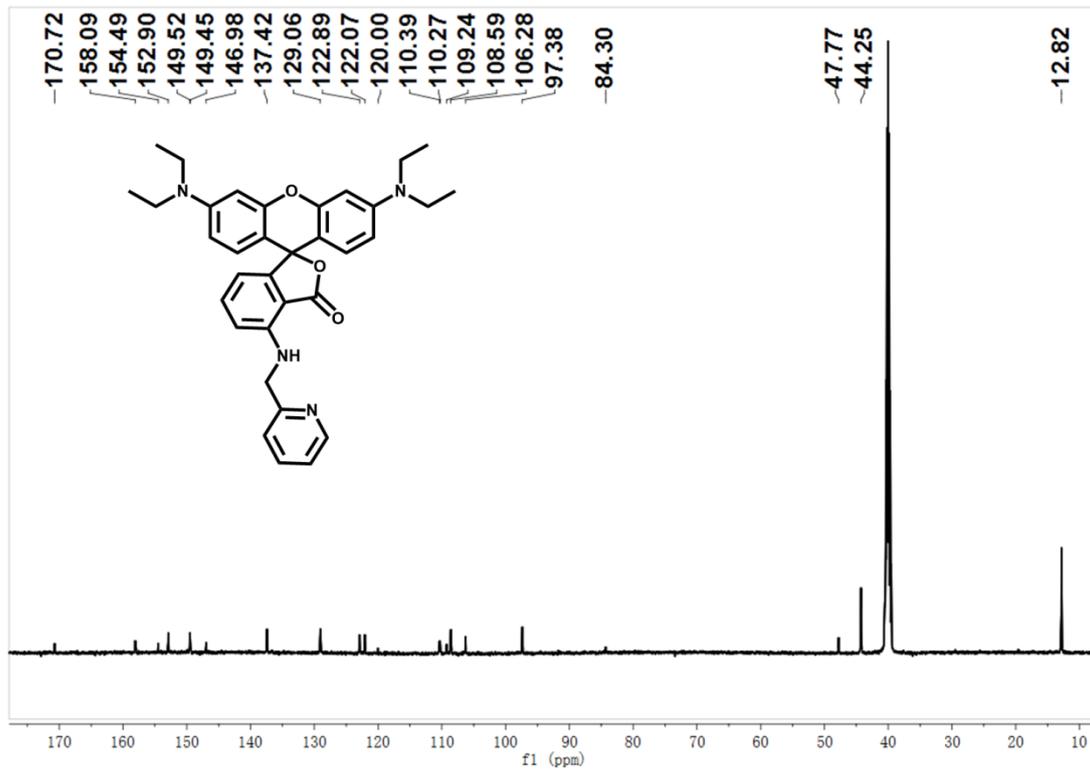


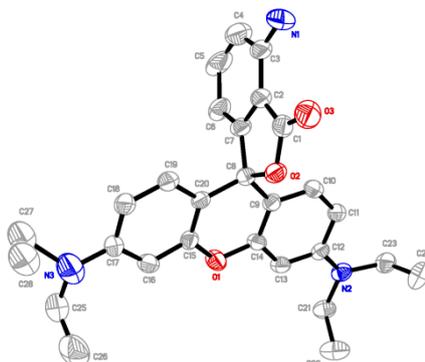
**Figure S11.** LC-MS spectra of (a) Rha-amino, from the spectrum of liquid chromatography, we can find the retention time was 2.7 min. (b) Rha-py, from the spectrum, we can find the retention time was 1.8 min. (c) The LC-MS spectra of Rha-py and  $\text{Ni}^{2+}$  in  $\text{CH}_3\text{CN}$  buffered with HEPES (9/1, v/v, pH=7.1, 20 mM) (HEPES buffer), from the spectrum, we can find the signal of HEPES and Rha-py, but no Rha-amino. (d) The LC-MS spectra of Rha-py and  $\text{Cu}^{2+}$  in HEPES buffer, from the spectrum, we can find the signal of HEPES and Rha-amino, but no Rha-py, which illustrated the probe was degraded by  $\text{Cu}^{2+}$  completely.











**Table S2.** Summary of crystal data and intensity collection parameters for Rha-amino.

The crystal data for Rha-amino was deposited into Cambridge Crystallographic Data Centre with CCDC numbers of 1036431.

| Compound  | Rha-amino   |
|---|---|
| Formula   | C <sub>28</sub> H <sub>31</sub> N <sub>3</sub> O <sub>3</sub> |
| Formula mass  | 457.56  |
| Space group   | P 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>                |
| <i>a</i> / Å  | 12.122(2)   |
| <i>b</i> / Å  | 13.002(3)   |
| <i>c</i> / Å  | 15.716(3)   |
| <i>α</i> / °  | 90  |
| <i>β</i> / °  | 90  |
| <i>γ</i> / °  | 90  |
| <i>V</i> / Å <sup>3</sup>                                       | 2476.9(9)   |
| <i>Z</i>  | 4   |
| <i>ρ</i> / g.cm <sup>-3</sup>                                   | 1.227   |
| <i>μ</i> / mm <sup>-1</sup>                                     | 0.080   |
| <i>F</i> <sub>000</sub>   | 976   |
| Temp, (K)   | 293(2)  |
| No. of collected reflns.  | 18290   |
| No. of unique reflns. (Rint)                                    | 4351(0.0636)  |
| Data/restraints/parameters                                      | 4351 / 29 / 311   |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [obs I > 2σ (I)] | 0.0831, 0.2154  |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)       | 0.1277, 0.2457  |
| Residual peak/ hole e.Å <sup>-3</sup>                           | 0.532/ -0.365   |
| Goodness-of-fit on F <sup>2</sup>                               | 1.063   |

## References

1. H. Kojima, M. Hirotsu, N. Nakatsubo, K. Kikuchi, Y. Urano, T. Higuchi, Y. Hirata and T. Nagano, *Anal. Chem.*, 2001, **73**, 1967.
2. Y. Liu, X. Dong, J. Sun, C. Zhong, B. Li, X. You, B. Liu and Z. Liu, *Analyst*, 2012, **137**, 1837.
3. H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.