

Supporting Information

A novel reversible fluorescent probe based on naphthalimide for sequential detection of aluminum (Al³⁺) and fluoride (F⁻) ions and its applications

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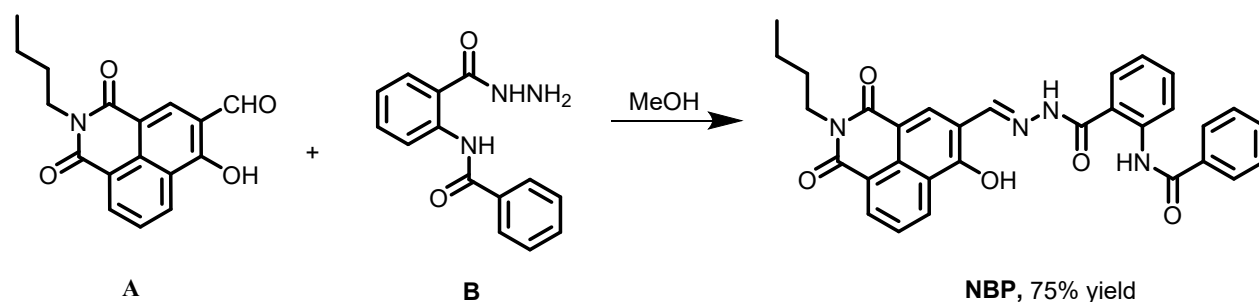
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1. General information

All reagents and solvents (analytical grade) were commercially available and used as received unless otherwise stated. The stock solutions including both metal solutions and anionic solutions were prepared in deionized water with a concentration of 0.2 mM. ^1H NMR spectra data were taken on Bruker-Advance DPX 400 MHz spectrometer with d_6 -DMSO as solvent. ESI-MS spectra were measured using an Agilent-6110 mass spectrometer. Fluorescent spectra were recorded on a Spectrofluorometer FS5. UV-vis spectra were obtained on a U3010-vis spectrophotometer. All the spectra were measured in DMSO/H₂O solution (9/1, v/v, pH 7.4, HEPES buffer, 0.2 mM) at room temperature with ex/em slit widths of 3.5 nm. FT-IR spectra were acquired in KBr with a Nicolet Nexus 470. Statistical analysis of the data was analysed by Origin 8. The pH values were measured on a digital pH meter by adjusting dilute hydrochloric acid or sodium hydroxide.

2. General method for the preparation of NBP

The precursors **A**¹⁻³ and **B**⁴ synthesized according to the published procedure. The synthetic strategy of probe **NBP** was summarized in Scheme S1



Scheme S1. Synthetic pathway of **NBP**

Synthesis of A

In a 100 mL round bottom flask, a mixture of *N*-butyl-4-hydroxy-1,8-naphthalimide (270 mg, 1.0 mmol) and hexamethylenetetramine (HMTA) (280 mg, 2 mmol) in trifluoroacetic acid (20 mL) was refluxed at 80 °C for 12 h, and then the solution was poured into ice water (200 mL), and the precipitate was filtered and

washed with distilled water several times. Subsequent the crude product was purified on silica gel (DCM / MeOH = 50 : 1) to give a yellow solid with 70% yield.

2-butyl-6-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinoline-5-carbaldehyde (A): yellow solid (325 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃) δ 13.12 (s, 1H), 10.06 (s, 1H), 8.69 – 8.66 (m, 3H), 7.77 – 7.73 (m, 1H), 4.13 – 4.09 (m, 2H), 1.68 – 1.63 (m, 2H), 1.43 – 1.35 (m, 2H), 0.91 (t, *J* = 0.8 Hz, 3H). ESI-MS *m/z*: [M]⁺ calcd. for C₁₇H₁₅NO₄ 297.1, found 297.0.

¹H NMR (CDCl₃)

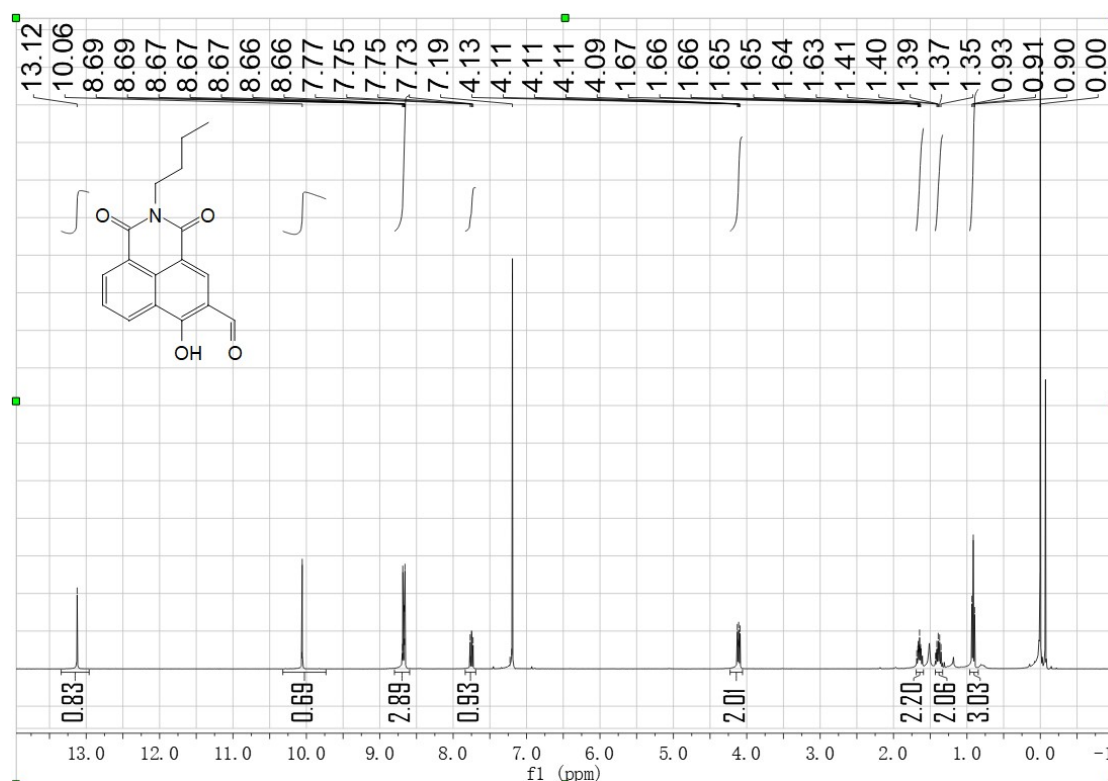


Fig. S1. ¹H NMR spectrum of A

Synthesis of B

To a stirred solution of 2-phenyl-4*H*-benzo[*d*][1,3]oxazin-4-one (223 mg, 1 mmol) in EtOH at room temperature, hydrazine (2 equiv.) was added. Then, the mixture was stirred at 65 °C for 3 h. After the reaction completed (monitored by TLC), the solvent was evaporated, and then the residue was purified by column chromatography on silica gel using EA/PE (v/v, 1/4) to afford pure product **B**.

***N*-(2-(hydrazinecarbonyl)phenyl)benzamide** (white solid, 85% yield, 0.22 g).

^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 12.57 (s, 1H), 10.21 (s, 1H), 8.66 (d, $J = 8.4$ Hz, 1H), 7.96 (d, $J = 8.4$ Hz, 2H), 7.78 (d, $J = 8.4$ Hz, 1H), 7.66 – 7.54 (m, 4H), 7.17 (t, $J = 8.4$ Hz, 1H), 4.69 (s, 2H). ESI-MS m/z : $[\text{M-H}]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2$ 255.1, found 254.9.

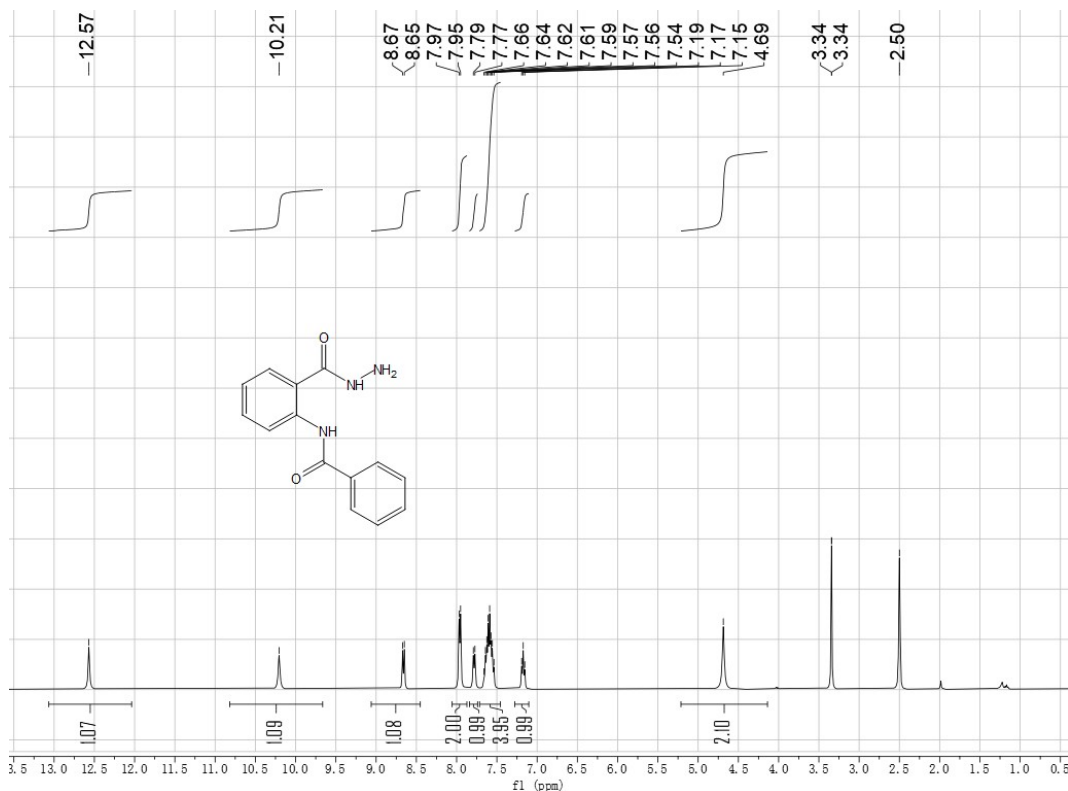


Fig. S2. ^1H NMR spectrum of **B**

Synthesis of NBP

In a 25 ml three-necked bottle, a mixture of 2-butyl-6-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinoline-5-carbaldehyde (**A**) (0.297 g, 1 mmol) and *N*-(2-(hydrazinecarbonyl)phenyl)benzamide (**B**) (0.255 g, 1 mmol) was dissolved in 10 ml of methanol and then the solution kept stirring at 70 °C for 2 h. After cooling to room temperature, the precipitate was filtered and washed with MeOH to obtain the crude product. Finally, the crude product was further purified through the recrystallization with $\text{DMSO}/\text{H}_2\text{O}$ mixture solution. (*E*)-*N*-(2-(2-((2-butyl-6-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinolin-5-yl)methylene)hydrazine-1-carbonyl)phenyl)benzamide (**NBP**) (yellow solid, 75% yield, 0.4 g). ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 14.14 (s, 1H), 12.82 (s, 1H), 11.77 (s, 1H), 8.89 – 8.86 (m, 1H),

8.70 – 8.67 (m, 1H), 8.60 (s, 1H), 8.53 – 8.50 (m, 2H), 7.99 – 7.94 (m, 3H), 7.89 – 7.84 (m, 1H), 7.70 – 7.64 (m, 3H), 7.35 – 7.31 (m, 1H), 4.06 – 4.02 (m, 2H), 1.65 – 1.58 (m, 2H), 1.40 – 1.32 (m, 2H), 0.93 (t, $J = 8.4$ Hz, 3H). ESI-MS m/z : $[M-H]^+$ calcd for $C_{31}H_{26}N_4O_5$ 534.1, found 532.9. IR (KBr cm^{-1}): 3433, 3243, 2955, 2350, 1690, 1654, 1598, 1324.

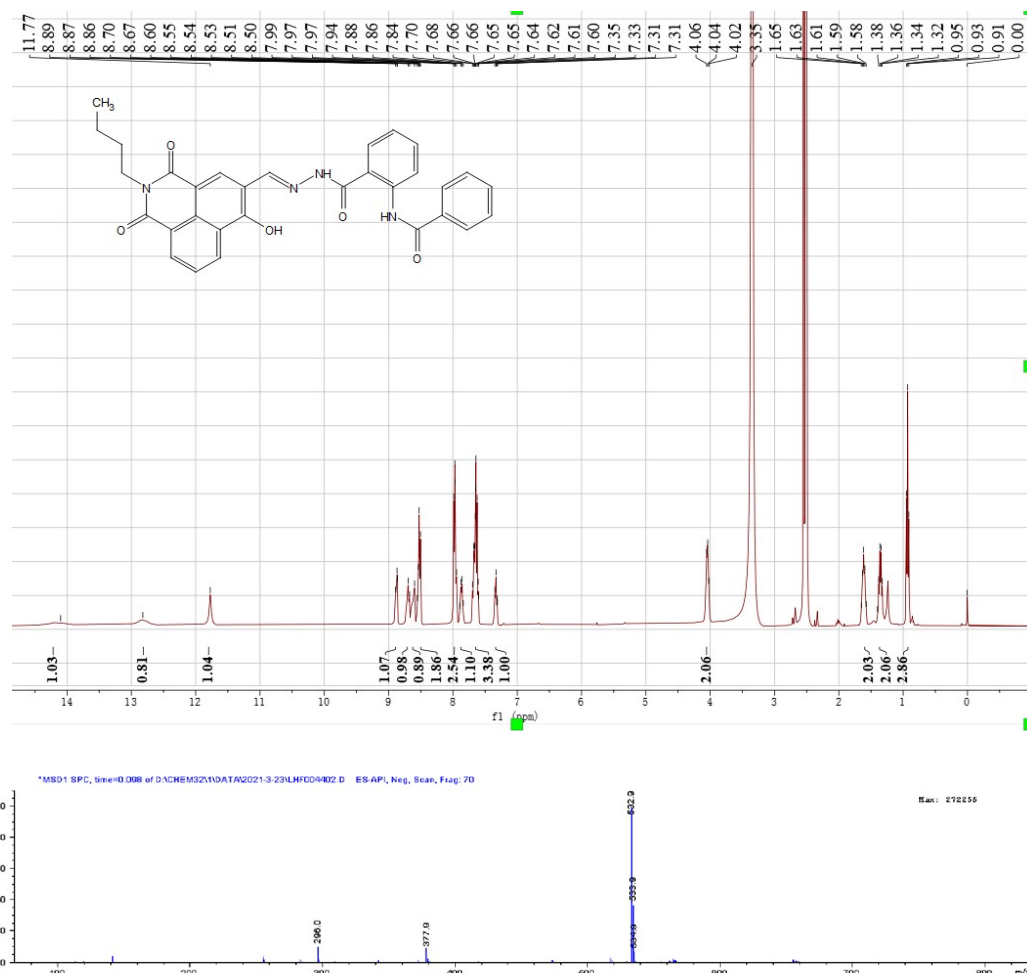


Fig. S3. NMR spectrum and MS of NBP

3. Solvent screening

The effect of mixture solvent systems (organic solvent/ H_2O , (9/1, v/v, pH 7.4, HEPES buffer, 0.2 mM) on the behavior of NBP in detecting Al^{3+} ions were investigated. Various organic solvents, including DMSO, MeOH, EtOH, Toluene, CH_3CN and THF were employed to prepare NBP solution (10 μM). As illustrated in Fig. S4, the fluorescence emission intensity was enhanced remarkably in DMSO/ H_2O solution (9/1, v/v, pH 7.4, HEPES buffer, 0.2 mM).

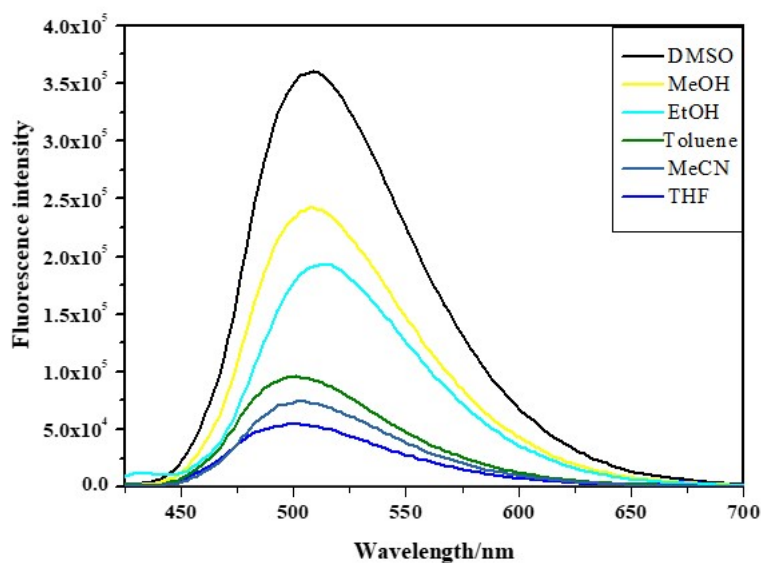


Fig. S4. The effect of solvent systems on the behavior of **NBP** in detecting Al^{3+}

4. The effect of pH values

To investigate the suitable pH value for the probe **NBP** in detecting Al^{3+} , the fluorescent intensities of **NBP** and **NBP- Al^{3+}** were measured in the range of pH 2.0 to 12.0 in DMSO/ H_2O solution (9/1, v/v, pH 7.4, HEPES buffer, 0.2 M) (Fig. S5). Free chemosensor **NBP** exhibited almost no changes in the fluorescence spectrum within pH range from 2 to 12. Nevertheless, the fluorescence signals of **NBP- Al^{3+}** was observed with large enhancement at the pH values 4.0 - 12.0 and its maximum emission intensity was achieved around pH = 8. No obvious fluorescence enhancement was observed under the strong acidic conditions (pH < 4), presumably owing to the abstraction of the protons of phenolic groups was suppressed and the protonation of nitrogen in C=N group, which was unfavorable for the complexation between **NBP** and Al^{3+} . In addition, the emission intensity gradually reduced under the alkaline conditions (pH > 8), which was ascribed to the formation of $\text{Al}(\text{OH})_4^-$ and thus led to a low concentration of **NBP- Al^{3+}** . These experimental results indicated that the optimized pH value range for **NBP- Al^{3+}** system was 7.0 – 9.0, revealing that **NBP** could be used as a good indicator for the detection of Al^{3+} ions under the biological environment.

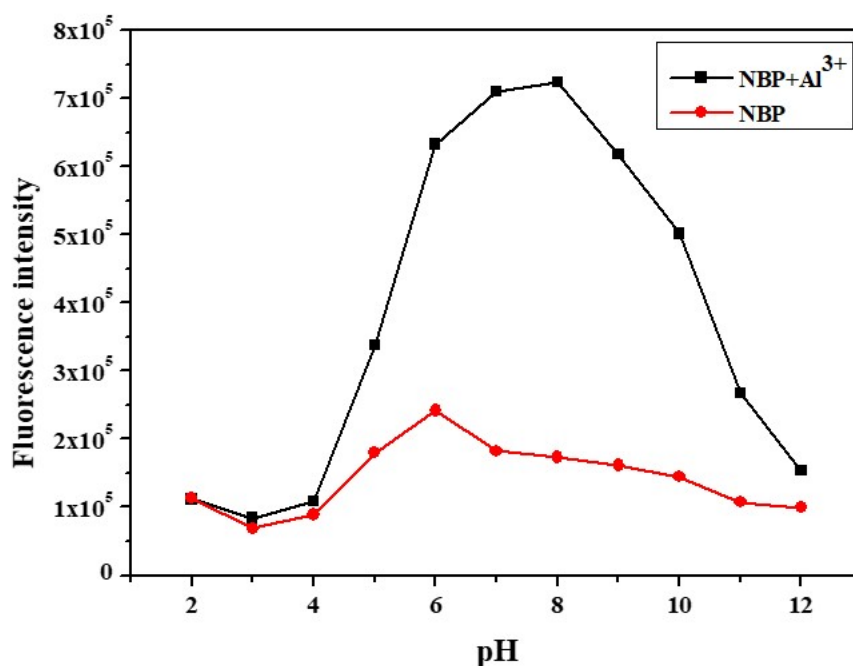


Fig. S5. The emission intensity at 513 nm of **NBP** (10 μ M) and **NBP-Al³⁺** in DMSO/H₂O solution at different pH values.

5. Reversibility study

Reversibility has proved to be one of the significant features to fabricate a novel fluorescence probe for practical applications. To investigate the reversible binding nature of **NBP** toward Al³⁺, various common anions like F⁻, HS⁻, NO₂⁻, S²⁻, S₂O₃²⁻, AcO⁻, SO₄²⁻, SO₃²⁻, Br⁻, CO₃²⁻, H₂PO₄⁻, HSO₄⁻, NO₃⁻, I⁻ and HCO₃⁻ were examined. As shown in Fig. S6, there were not finding any fluorescence emission changes to the above anions for **NBP-Al³⁺**, except for F⁻. F⁻ ions induced obvious fluorescence quenching at 513 nm through the decomplexation of the **NBP-Al³⁺** complex.

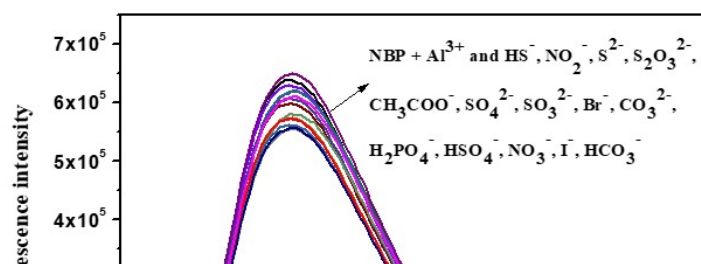


Fig. S6. Fluorescence spectra of **NBP**- Al^{3+} with various anions (5 equiv.)

6. Binding association constant

According to the Benesi-Hildebrand equation (Fig. S7), the binding constant (K) of **NBP** toward Al^{3+} was determined to be $4.22 \times 10^{10} \text{ M}^{-1/2}$ on the basis of the fluorescence titration experiments.

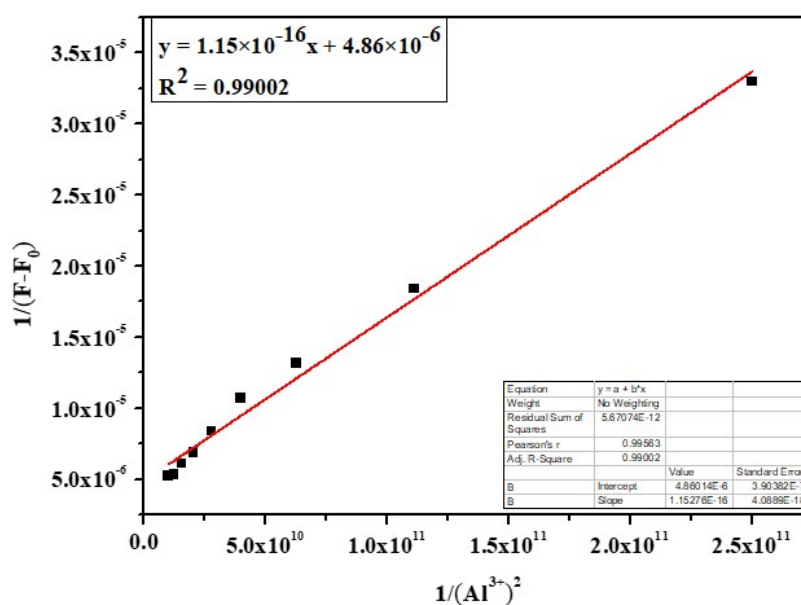


Fig. S7. Benesi-Hildebrand curve of $1/[\text{Al}^{3+}]^2$ vs $1/(F-F_0)$ based on stoichiometry **NBP**- Al^{3+} complex (1:2) ($\lambda_{\text{ex}} = 403 \text{ nm}$, $\lambda_{\text{em}} = 513 \text{ nm}$, probe conc. $10 \mu\text{M}$)

7. References

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