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# **Supporting Information For**

# Rational design of a highly sensitive and selective "turn-on" fluorescent sensor for PO<sub>4</sub><sup>3-</sup> detection

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Fig. S1. Excitation and emission spectra of of P in THF–water (9.5:0.5, v/v) solution.



**Fig. S2.** Fluorescence spectra of **P**  $(1.0 \times 10^{-4} \text{ M})$  in the presence of different concentration of Fe<sup>3+</sup>  $(0-2.0 \times 10^{-4} \text{ M})$  in THF–water (9.5:0.5, v/v) solution. Inset: Fluorescence intensity at 531 nm as a function of Fe<sup>3+</sup> concentration.



**Fig. S3.** (a) Fluorescence emission data of **P** ( $1.0 \times 10^{-4}$  M) with various metal ions (Fe<sup>3+</sup>, Cu<sup>2+</sup>, Ag<sup>+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Fe<sup>2+</sup>, Ba<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Na<sup>+</sup>, Co<sup>2+</sup> and Cr<sup>3+</sup>,  $2.0 \times 10^{-3}$  M) in THF–water (9.5:0.5, v/v) solution ( $\lambda_{ex} = 468$  nm). (b) Color and fluorescent changes of **P** upon the addition of various metal ions. Photographs were taken under (top) 365 nm UV light and (bottom) daylight illumination, respectively.



**Fig. S4.** UV–vis titration spectra of **P** ( $5.0 \times 10^{-5}$  M) with increasing amounts of Fe<sup>3+</sup> in THF–water (9.5:0.5, v/v) solution. Inset: plots of the absorption ratio (A<sub>333 nm</sub>/A<sub>450 nm</sub>) of **P** versus the concentration of Fe<sup>3+</sup> ions.



Fig. S5. Job's plots of the complexation between P and Fe<sup>3+</sup>. Total concentration of P and Fe<sup>3+</sup> was kept constant at 20  $\mu$ M.



**Fig. S6.** Benesi–Hildebrand plot (emission at 468 nm) of **P** by plotting  $1/(F_0 - F)$  as a function of  $1/[Fe^{3+}]$ .

The association constant (Ka) of P-Fe<sup>3+</sup> complex was calculated by the Benesi– Hildebrand Eq.:

$$\frac{1}{F_0 - F} = \frac{1}{K_a \times (F_0 - F_{\min}) \times [\text{Fe}^{3+}]^n} + \frac{1}{F_0 - F_{\min}}$$

where *F* is the fluorescence intensity at 530 nm at any given Fe<sup>3+</sup> concentration,  $F_0$  is the fluorescence intensity at 530 nm in the absence of Fe<sup>3+</sup>, and  $F_{min}$  is the minimum fluorescence intensity at 530 nm in the presence of Fe<sup>3+</sup> in solution. The association constant  $K_a$  was evaluated graphically by plotting  $1/(F_0 - F)$  against  $1/[Fe^{3+}]$ . Data were linearly fitted according to Eq. and the K<sub>a</sub> value was  $9.46 \times 10^3$  M<sup>-1</sup>



Fig. S7. Chemical structures of P1, P2 and P3.



**Fig. S8.** Fluorescence spectra changes of **P**, **P1**, **P2** and **P3** solution  $(1.0 \times 10^{-4} \text{ M})$  upon addition of 20 equiv. of Fe<sup>3+</sup> in THF–water (9.5:0.5, v/v).

## The binding site of compound P

As shown in Fig. S7, the compounds **P2** and **P3** contain the binding site of B and A, which is same as that of **P**, respectively. However, such binding site A or B is absent in compound **P1**. The Fe<sup>3+</sup> ions have been also added into the solutions of compounds **P1**, **P2** and **P3** for the better comparison. Under the same experimental conditions, no

obvious emission changes are observed for P1 and P2 upon addition of  $Fe^{3+}$ , however, P3 exhibits evident emission quenching phenomenon, as shown in Fig. S8. Therefore, we can conclude that the binding sites between P and  $Fe^{3+}$  should occur on the point A.



**Fig. S9.** Plot of the intensity at 531 nm for a mixture of **P**–Fe<sup>3+</sup> and PO<sub>4</sub><sup>3–</sup> in THF– water (9.5:0.5, v/v) solution in the range 0–20.0  $\mu$ M ( $\lambda$ ex = 468 nm).

# The result of the analysis as follows:

Linear Equation: 
$$Y = 0.55773 \times X + 3.95$$
 R = 0.9972  
 $S = 5.577 \times 10^5$   $\sigma = \sqrt{\frac{\sum (F_0 - \overline{F_0})^2}{N - 1}} = 0.320$  (N=10) K=3  
LOD = K ×  $\delta$  / S = 1.721×10<sup>-6</sup> M

 $F_0$  is the fluorescence intensity of **P**–Fe<sup>3+</sup>.

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**Fig. S10.** Fluorescence intensity of **FeP** after addition of  $PO_4^{3-}$  (black) at 531 nm and followed by adding 100 equiv of other cations and anions (red) or their mixtures.



**Fig. S11.** Fluorescent "OFF–ON–OFF" cycles of **FeP** in THF–water (9.5:0.5, v/v) mixture, controlled by the alternative addition of Fe<sup>3+</sup> and PO<sub>4</sub><sup>3–</sup>.



**Fig. S12** Plot of the intensity at 531 nm for a mixture of **P** and Fe<sup>3+</sup> in THF–water (9.5:0.5, v/v) solution in the range 0–2.5  $\mu$ M ( $\lambda$ ex = 468 nm).

# The result of the analysis as follows:

Linear Equation: 
$$Y = -13.94545 \times X + 249.94$$
 R = 0.9920  
S =  $1.39 \times 10^7 \sigma = \sqrt{\frac{\sum (F_0 - \overline{F_0})^2}{N-1}} = 5.940$  (N=10) K=3  
LOD = K ×  $\delta$  / S =  $1.282 \times 10^{-6}$  M

 $F_0$  is the fluorescence intensity of **P**.

#### **Experimental**

#### 1. Materials and instruments

All reagents and solvents were commercially available at analytical grade and were used without further purification. 4-bromo-1,8-naphthalic anhydride was purchased from Sigma-Aldrich. The solutions of ions were prepared from FeCl<sub>3</sub>·6H<sub>2</sub>O, CaCl<sub>2</sub>, CdCl<sub>2</sub>, MnCl<sub>2</sub>·4H<sub>2</sub>O, NaCl, ZnCl<sub>2</sub>, KCl, AgNO<sub>3</sub>, CuCl<sub>2</sub>, FeSO<sub>4</sub>·7H<sub>2</sub>O, BaCl<sub>2</sub>·2H<sub>2</sub>O, KCl, MgCl<sub>2</sub>·6H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, ZnCl<sub>2</sub>, NaF, NaCl, NaBr, KI, NaNO<sub>3</sub>, CH<sub>3</sub>COONa, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub> respectively. All solutions are used in ultra-pure water purified by a Millipore water purification system.

<sup>1</sup>H NMR was recorded on a Bruker 400 spectrometer. The UV–vis absorption spectra were recorded on a Shimadzu UV-3600 scanning spectrophotometer. The fluorescence spectra were recorded on a Shimadzu RF-5301 spectrophotometer.

(uncorrected). LC-MS was performed on an Agilent 1200/6220 spectrometer. Melting points were measured on an X-4 digital melting-point apparatus, all melting points were uncorrected.

#### 2. Measurement of fluorescence quantum yields

Fluorescence quantum yields were determined by the following equation.

$$\Phi = \frac{n_x^2}{n_{stad}^2} \frac{F_x}{F_{stad}} \Phi_{fstad}$$

Where  $\Phi$  is fluorescence quantum yield; F is the integrated fluorescence intensity; n is the refractive index of solvent. The subscript *stad* refers to the reference of quinine sulphate and the value of  $\Phi_{fstad}$  is 0.55.

# 3. The details about the reversible experiment

The fluorescent "OFF-ON-OFF" cycles of sensor **FeP** are controlled by the alternative addition of  $PO_4^{3-}$  and  $Fe^{3+}$  ions. The reversible experiments were carried out by adding 30 equivalents of  $PO_4^{3-}$  into 20 mL of a solution of **FeP** ( $1.0 \times 10^{-4}$  M, THF/water = 9.5: 0.5, v:v) using a micropipette, and then about 30 equivalents of  $Fe^{3+}$  ions was added into the above solution. The each of test solutions was stirred for 1 min and immediately added into a quartz cuvette of 1 cm optical path length for the fluorescent measurement.

#### 4. Synthesis and characterization

Synthesis of 4-hydrazino-N-amino-1,8-naphthalimide

![](_page_8_Figure_10.jpeg)

Scheme 1 Synthetic routes of compound P.

4-bromo-1, 8-Naphthalene anhydride (278 mg, 1.0 mmol) were firstly dissolved in Butoxyethanol (10 mL), Then, hydrazine hydrate (80% w/w, 120 mg, 10.0 mmol) was added into the above solution (Scheme 1). The solution was stirred under reflux and N<sub>2</sub> atmosphere conditions for 4 h, after cooling to room temperature, the yellow precipitate was filtrated, washed with water three times, then recrystallized with [v(DMF):v(acetonitrile) = 1:1] to get dark red powdery product (yield: 92%). m.p.285°C~286 °C.<sup>1</sup>H NMR (DMSO, 400 MHz, TMS)  $\delta$  (ppm) 9.19 (s, 1H), 8.63 (d, J = 8.4 Hz, 1H), 8.43 (d, J = 7.2 Hz, 1H), 8.29 (d, J = 8.4 Hz, 1H), 7.65 (dd, J<sub>1</sub> = 7.6Hz, J<sub>2</sub> = 8.0 Hz, 1H), 7.25 (d, J=8.4 Hz, 1H), 5.73 (s, 2H), 4.70 (s, 2H).

#### Synthesis of compound P

4-hydrazino-N-amino-1,8-naphthalimide (120 mg, 0.5 mmol), salicylic aldehyde (120 mg, 10 mmol) and catalytic amount of acetic acid were combined in hot absolute ethanol (15 mL) (Scheme 1). The solution was stirred under reflux conditions for 2 h, after cooling to room temperature, the red precipitate was filtrated, washed with hot absolute ethanol three times, The obtained sensor compound **P** was isolated by column chromatography as a yellow residue (yield: 85%). m.p.>300 °C. <sup>1</sup>H NMR (DMSO, 400 MHz, TMS)  $\delta$  (ppm) 11.55 (s, 1H), 11.16 (s, 1H), 10.25 (s,1H), 9.00 (s, 1H), 8.87 (d, J = 8.4Hz, 1H), 8.82 (s, 1H), 8.53 (d, J = 6.8Hz, 1H), 8.42 (d, J = 8.8Hz, 1H), 7.86 (d, J = 7.6Hz, 1H), 7.83 (dd, J<sub>1</sub> = 8.0Hz, J<sub>2</sub> = 8.0Hz, 1H), 7.68 (d, J = 8.8Hz, 1H), 7.51 (dd, J<sub>1</sub> = 8.4Hz, J<sub>2</sub> = 7.2Hz, 1H), 7.28 (dd, J<sub>1</sub> = 7.2Hz, J<sub>2</sub> = 7.2Hz 1H), 7.05 (dd, J<sub>1</sub> = 8.0Hz, J<sub>2</sub> = 7.2Hz, 2H), 6.96 (dd, J<sub>1</sub> = 8.0Hz, J<sub>2</sub> = 7.2Hz, 2H). ESI-MS m/z (M-H<sup>+</sup>):calcd, 451.14; found, 451.1.

![](_page_10_Figure_1.jpeg)

Scheme 1. Synthetic route to compound P1.

#### Synthesis of compound P1

4-hydrazino-*N*-amino-1, 8-naphthalimide (120 mg, 0.5 mmol), aniline (930 mg, 10.0 mmol) and catalytic amount of acetic acid were combined in absolute ethanol (15 mL). The solution was stirred under reflux conditions for 2 h, after the mixture was cooled to room temperature, the red precipitate was filtrated and washed with hexane (3×10 mL), then dried overnight at 60 °C in a vacuum oven to give **P1** (yield: 87.0%). <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 400 MHz, TMS)  $\delta$  (ppm) 11.56 (s, 1H), 8.87 (d, *J* = 8.5 Hz, 1H), 8.73 (s, 1H), 8.54 (d, *J* = 7.2 Hz, 1H), 8.50 (s, 1H), 8.44 (d, *J* = 8.6 Hz, 1H), 7.97 (d, *J* = 7.4 Hz, 2H), 7.86 – 7.78 (m, 4H), 7.65 – 7.57 (m, 3H), 7.51 – 7.43 (m, 3H).

![](_page_10_Figure_5.jpeg)

Scheme 2. Synthetic route to compound P2.

#### Synthesis of Inter–M1

4-bromo-1, 8-naphthalic anhydride (500 mg, 1.8 mmol) and *N*-octylamine (468 mg, 3.6 mmol) were dissolved in ethanol (100 mL). The solution was stirred under reflux conditions for 10 h. After cooling to room temperature, the yellow sediments were collected by filtration and then dried overnight at 60 °C in a vacuum oven to give **Inter–M1** (yield: 89%). <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 400 MHz, TMS)  $\delta$  (ppm) 8.56 (t, *J* = 8.6 Hz, 2H), 8.34 (d, *J* = 7.9 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 8.00 (t, *J* = 7.9 Hz, 1H), 4.02 (t, *J* = 7.3 Hz, 2H), 1.67 – 1.55 (m, 2H), 1.31 – 1.24 (m, 10H), 0.85 (t, *J* = 6.0 Hz, 3H).

## Synthesis of Inter-M2

Compound Inter–M1 (390 mg, 1.0 mmol) was dissolved in butoxy ethanol (20 mL), then, hydrazine hydrate (80% w/w, 187 mg, 3.0 mmol) was added into the above solution and the solution was refluxed for 2h. After cooling to room temperature, the yellow powders were filtered and washed with water (3×30 mL). Then dried overnight at 60 °C in a vacuum oven to give Inter–M2 (yield: 91%). <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 400 MHz, TMS)  $\delta$  (ppm) 9.10 (s, 1H), 8.61 (d, *J* = 8.4 Hz, 1H), 8.41 (d, *J* = 7.3 Hz, 1H), 8.28 (d, *J* = 8.6 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 1H), 4.66 (s, 2H), 4.00 (t, *J* = 7.4 Hz, 2H), 1.60 – 1.59 (m, 2H), 1.30 – 1.23 (m, 10H), 0.84 (t, *J* = 6.4 Hz, 3H).

#### Synthesis of compound P2

Compound Inter–M2 (136 mg, 0.4 mmol) was dissolved in absolute ethanol (20 mL). An excess of salicylic aldehyde (442 mg, 4.0 mmol) and catalytic amount of acetic acid were added and the mixture was refluxed for 2 h. After the mixture was cooled to room temperature, the precipitate produced was filtered and recrystallized with ethanol to give a yellow solid P2 (yield: 78%.) <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 400 MHz, TMS)  $\delta$  (ppm) 11.46 (s, 1H), 10.24 (s, 1H), 8.81 (s, 2H), 8.47 (d, J = 6.8 Hz, 1H),

8.37 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.79 (t, J = 7.8 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 6.95 - 6.90 (m, 2H), 4.00 (t, J = 7.1 Hz, 2H),
3.33 (s, 5H), 1.61 (s, 2H), 1.30 - 1.23 (m, 10H), 0.84 (t, J = 5.8 Hz, 3H).

![](_page_12_Figure_2.jpeg)

Scheme 3. Synthetic route to compound P3

#### Synthesis of compound Inter–M3

4-bromo-1, 8-naphthalic anhydride (750 mg, 2.7 mmol) was added to ethanol (50 mL) and heated to reflux, then, hydrazine hydrate (80% w/w, 168 mg, 2.7 mmol) was added into the above solution and the solution was refluxed for overnight. After the mixture was cooled to room temperature, the precipitate produced was filtered and washed with ethanol, Then dried overnight at 60 °C in a vacuum oven to give faint yellow solid **Inter–M3** (yield: 95%). <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 300 MHz)  $\delta$  (ppm) 8.66 – 8.49 (m, 2H), 8.40 – 8.29 (m, 1H), 8.28 – 8.16 (m, 1H), 8.08 – 7.94 (m, 1H), 5.81 (s, 2H).

# Synthesis of compound Inter-M4

Compound Inter–M3 (292 mg, 1.0 mmol) and *N*-octylamine (258 mg, 2.0 mmol) were added into butoxy ethanol (20 mL) and refluxed for 3 h. After the mixture cooled to room temperature, poured into 100 mL water, the precipitated solids were filtered, dried overnight at 60 °C in a vacuum oven to give red solid Inter–M4 (yield: 92.0%). <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 300 MHz)  $\delta$  (ppm) 8.73 (d, *J* = 8.0 Hz, 1H), 8.45 (d, *J* =

7.0 Hz, 1H), 8.27 (d, *J* = 8.3 Hz, 1H), 7.84 (s, 1H), 7.69 (t, *J* = 7.1 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 5.73 (s, 2H), 3.43 – 3.33 (m, 2H), 1.79 – 1.61 (m, 2H), 1.51 – 1.16 (m, 10H), 0.85 (s, 3H).

# Synthesis of compound P3

Compound Inter–M4 (136 mg, 0.4 mmol) was dissolved in absolute ethanol (20 mL). An excess of salicylic aldehyde (442 mg, 4 mmol) and catalytic amount of acetic acid were added and the mixture was refluxed for 2 h. After the mixture was cooled to room temperature, the precipitate produced was filtered and washed with hexane (3 ×10 mL), dried in vacuum to give a yellow solid P3 (Yield: 90%). <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 300 MHz)  $\delta$  (ppm) 11.19 (s, 1H), 8.99 (s, 1H), 8.78 (d, *J* = 8.2 Hz, 1H), 8.49 (d, *J* = 7.1 Hz, 1H), 8.31 (d, *J* = 8.6 Hz, 1H), 7.91 (t, *J* = 4.9 Hz, 1H), 7.81 – 7.68 (m, 2H), 7.51 – 7.45 (m, 1H), 7.05 – 6.99 (m, 2H), 6.83 (d, *J* = 8.7 Hz, 1H), 3.43 – 3.37 (m, 2H), 1.74-1.68 (m, 2H), 1.42 – 1.26 (m, 10H), 0.88 (t, *J* = 6.6 Hz, 3H).