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Supplementary Material

Turn-on fluorescence detection of pyrophosphate anion based on DNA-attached cobalt oxyhydroxide

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Contents

Experimental section

Materials and reagents

DNA oligonucleotide (F-DNA: 5`-FAM-GGAAGGAAAAACGTTGG-3`) was HPLC purified and purchased from Sangon Biotech Co., Ltd. (Shanghai, China). Tris (hydroxymethyl) aminomethane (Tris), glycine (Gly), and alanine (Ala) were purchased from Aladdin Reagents Co., Ltd. (Shanghai, China). The oligonucleotide was resuspended to 100 μM and stored in Tris-HCl buffer (10 mM, pH 7.4). Adenosine monophosphate (AMP), adenosine diphosphate (ADP), adenosine triphosphate (ATP), adenine (A), and thymine (T) were purchased from Sangon Biotech Co., Ltd. (Shanghai, China). Glucose (Glu) and fructose (Fru) were purchased from Sigma-Aldrich Co., Ltd. (Buchs, German). Aqueous solutions of $P_2O_7^{4-}$, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, HCO_3^-, CO_3^{2-}, SO_4^{2-}, S^{2-}, NO_3^-, Ac^-, and Cl^- were prepared from $Na_4P_2O_7$, $NaH_2PO_4{\cdot}2H_2O$, $Na_2HPO_4{\cdot}2H_2O$, $Na_3PO_4{\cdot}12H_2O$, $NaHCO_3$, Na_2CO_3, Na_2SO_4, Na_2S, $NaNO_3$, NaAc, and NaCl, respectively. Aqueous solutions of Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, and Zn^{2+} were prepared from NaCl, KCl, $MgCl_2{\cdot}6H_2O$, $CaCl_2{\cdot}2H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, and $Zn(NO_3)_2{\cdot}6H_2O$, respectively. And the above inorganic salts were of analytical reagent grade and purchased from Chengdu Kelong Chemical Reagents Factory (Chengdu, China). All solutions in this experiment were prepared using ultrapure water with a specific resistance of 18.2 MΩ cm.

Apparatus

Fluorescence measurements were performed using a Hitachi F-4500 spectrofluorophotometer (Tokyo, Japan). Fluorescence emission spectra were measured at an excitation wavelength of 490 nm with an emission maximum at 518 nm. UV-Vis absorption spectra were recorded on a UV-vis

2450 spectrophotometer (Shimadzu, Japan). The transmission electron microscope (TEM) images were achieved using an FEI Tecnai G2 F20 (USA). The Fourier transform infrared (FT-IR) spectrum was measured in KBr pellet with a Bruker IFS 113v spectrometer (Germany). Zeta potential was measured by a Malvern Zetasizer Nano-ZS (UK).

The preparation of CoOOH nanoflakes

CoOOH nanoflakes were prepared according to a previously published method.[1] Briefly, 250 μL of a 1.0 M sodium hydroxide solution was added to a vial and mixed with 1.0 mL of cobaltous nitrate ($Co(NO_3)_2$, 10 mM) solution. After sonicating for 1 min, 50 μL of 0.9 M sodium hypochlorite was added. Then, the solution was sonicated for 10 min. The obtained nanoflakes were washed by ultracentrifugation three times and finally dispersed in 2 mL of ultrapure water.

Fluorescence sensing PPi

The PPi detection was performed through competitive interaction. First, 7.5 μL of 5 μM F-DNA was added to 470 μL of Tris-HCl buffer (10 mM, pH 7.4). Next, 7.5 μL of 0.25 mg mL^{-1} CoOOH nanoflakes and 10 μL of $MgCl_2$ (0.5 M) were mixed with the above solution, followed by incubation at room temperature for 15 min. Afterward, 5 μL of PPi with different concentrations was added and incubated at room temperature for 30 min. Finally, the resulting solution was detected by fluorescence with the maximum excitation and emission wavelengths of 490 and 518 nm, respectively.

Table S1 Summary of different fluorescent PPi assays.

Probe	Detection limit (μM)	Linear range (μM)	Ref.
$Al(QS)_2Cl$[a]	0.023	0.16 – 10	2
Gold nanoparticles	–	0.13 – 1300	3
FAM-labelled DNA	0.04	0.4 – 40	4
FAM-labelled DNA	0.076	0.2 – 4	5
Tetraphenylethylene moiety	0.9	0 – 60	6
Dinuclear Zn^{2+} complex	1	–	7
Rhodamine derivative	7.3	0 – 400	8
FAM-labelled DNA	0.3	0 – 10	This work

[a] $Al(QS)_2Cl$: bis(8-hydroxy quinoline-5-solphonat) chloride aluminum (III).

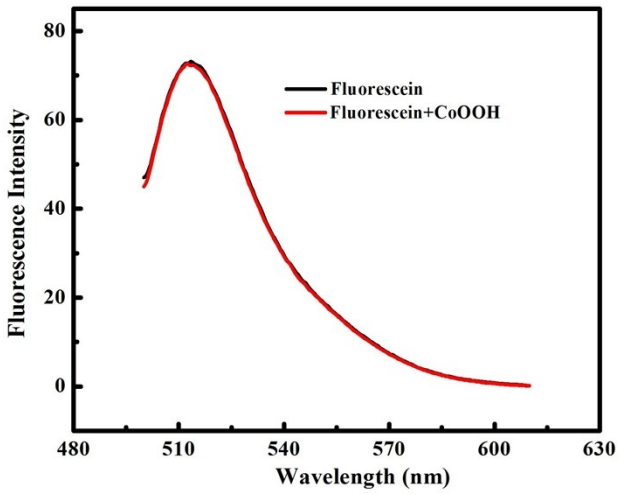

Fig. S1. Fluorescence spectra of fluorescein with and without CoOOH nanoflakes. Concentrations: fluorescein (10 μM) and CoOOH nanoflakes (3.75 μg mL^{-1}).

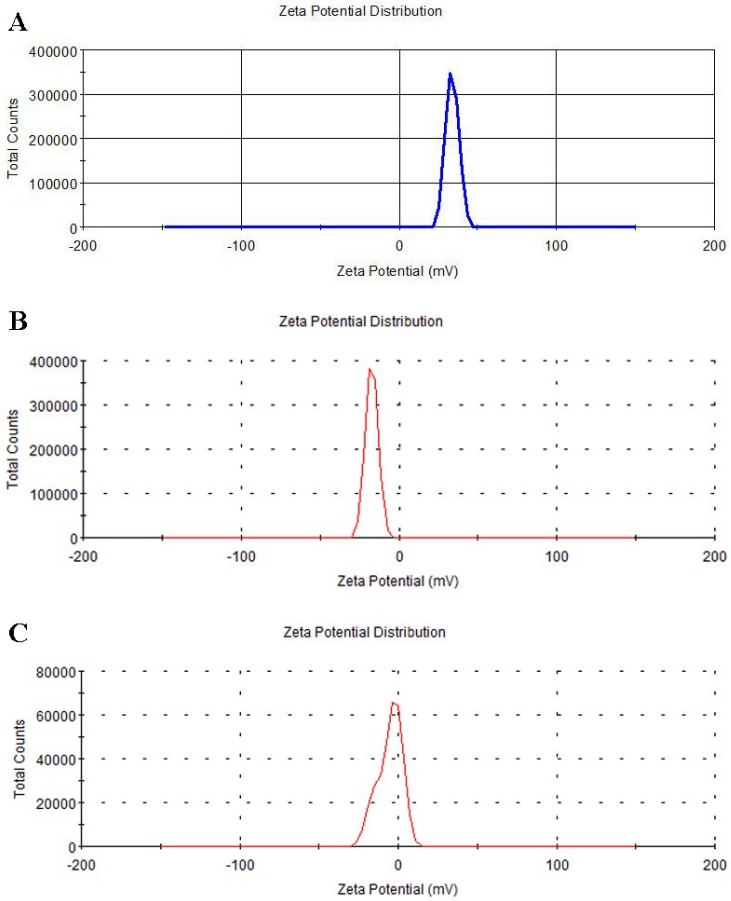

Fig. S2. The ζ potential of CoOOH nanoflakes (A), DNA-CoOOH nanoflake complex (B), and PPi-CoOOH nanoflake complex (C). Concentrations: CoOOH nanoflakes (18.75 μg mL^{-1}), F-DNA (375 μM), and PPi (50 μM).

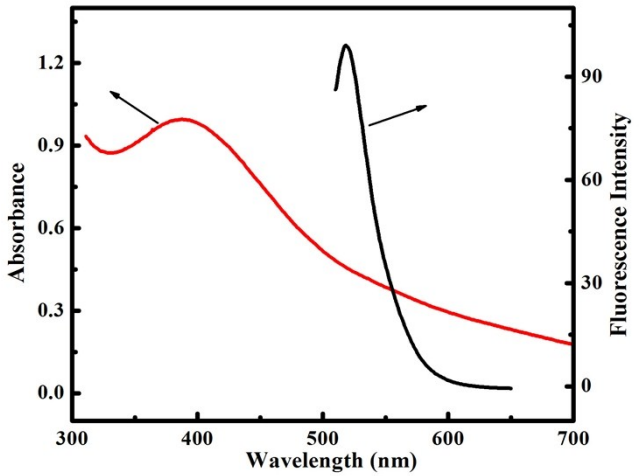

Fig. S3. UV-Vis absorption spectrum of CoOOH nanoflakes and the fluorescence emission spectrum of F-DNA. Concentrations: CoOOH nanoflakes (3.75 μg mL^{-1}) and F-DNA (75 μM).

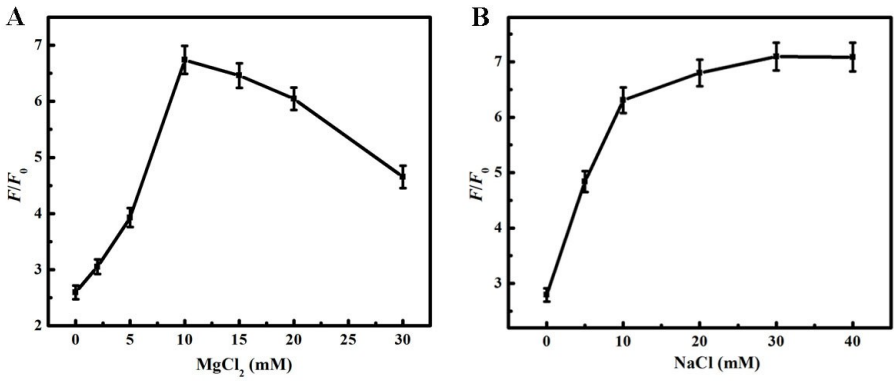

Fig. S4. The fluorescence intensity of F-DNA/CoOOH nanoflake system with the addition of different concentrations of $MgCl_2$ (A) and NaCl (B). Here, F and F_0 are the fluorescence intensities with and without the target, respectively. Concentrations: F-DNA (75 μM), CoOOH nanoflakes (3.75 μg mL^{-1}), and PPi (10 μM).

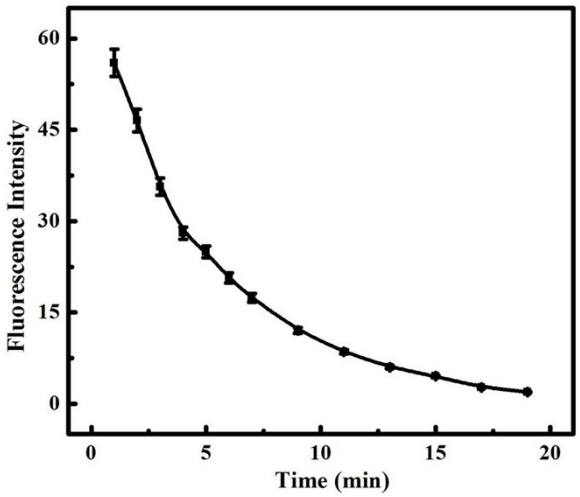

Fig. S5. Time-dependent fluorescence responses of F-DNA with CoOOH nanoflakes. Concentrations: F-DNA (75 μM), CoOOH nanoflakes (3.75 μg mL^{-1}), and $MgCl_2$ (10μM).

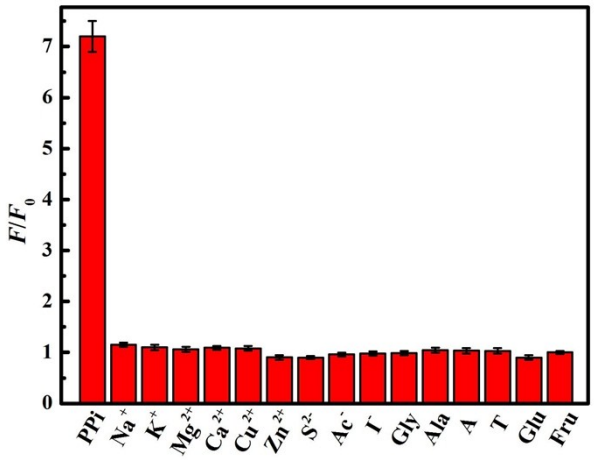

Fig. S6. Relative fluorescence intensity (F/F_0) of the system in the presence of PPi and other potential interferents. The concentrations of PPi and potential interferents were all 10 μM. Here, F and F_0 are the fluorescence intensities with and without the target, respectively. Concentrations: F-DNA (75 μM) and CoOOH nanoflakes (3.75 μg mL^{-1}).

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