Supporting Information

Highly efficient fluorescence sensing of phosphate by dual-emissive lanthanide MOFs

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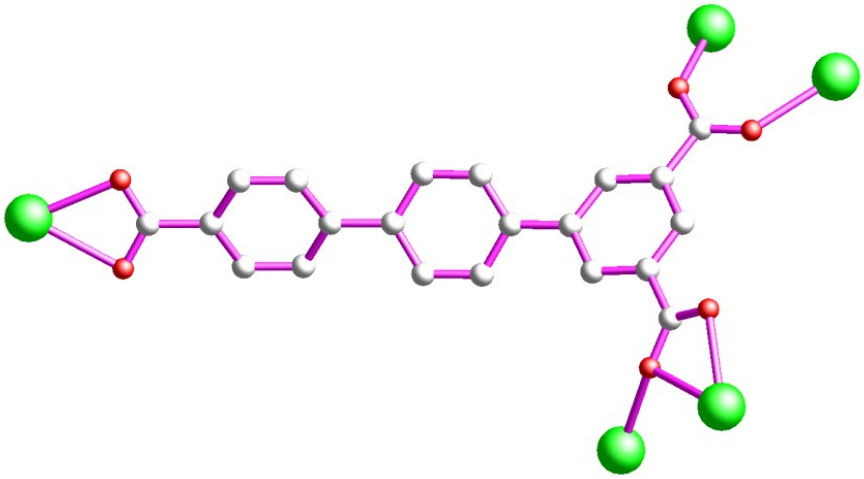

Scheme S1 The full de-protonated L^{3-} ligand adopts μ_7-η_1, η_1, η_2, η_1, η_1 and η_1 coordination mode.

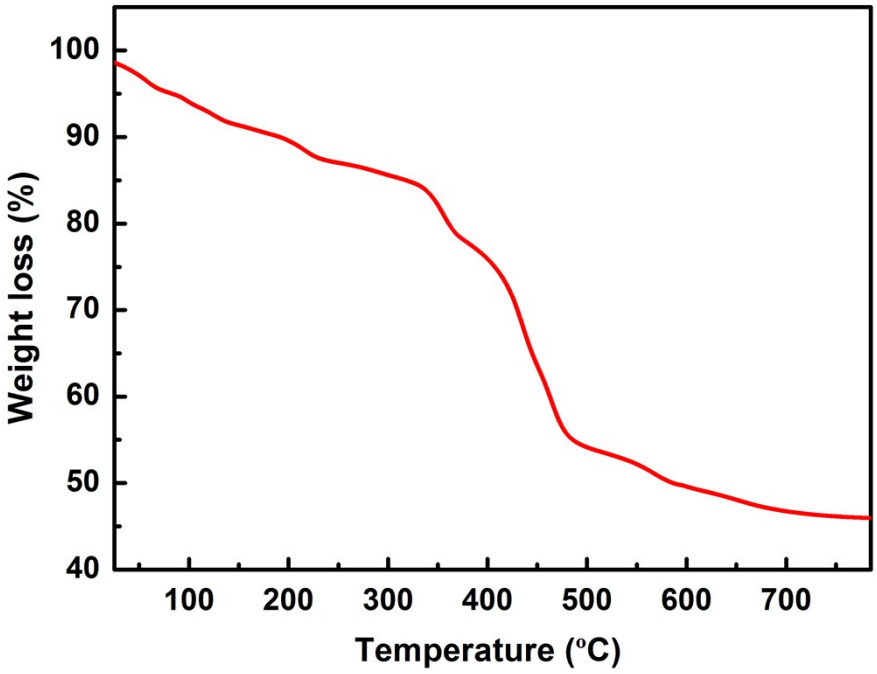

Fig. S1 TGA profile for the as-synthesized **1**.

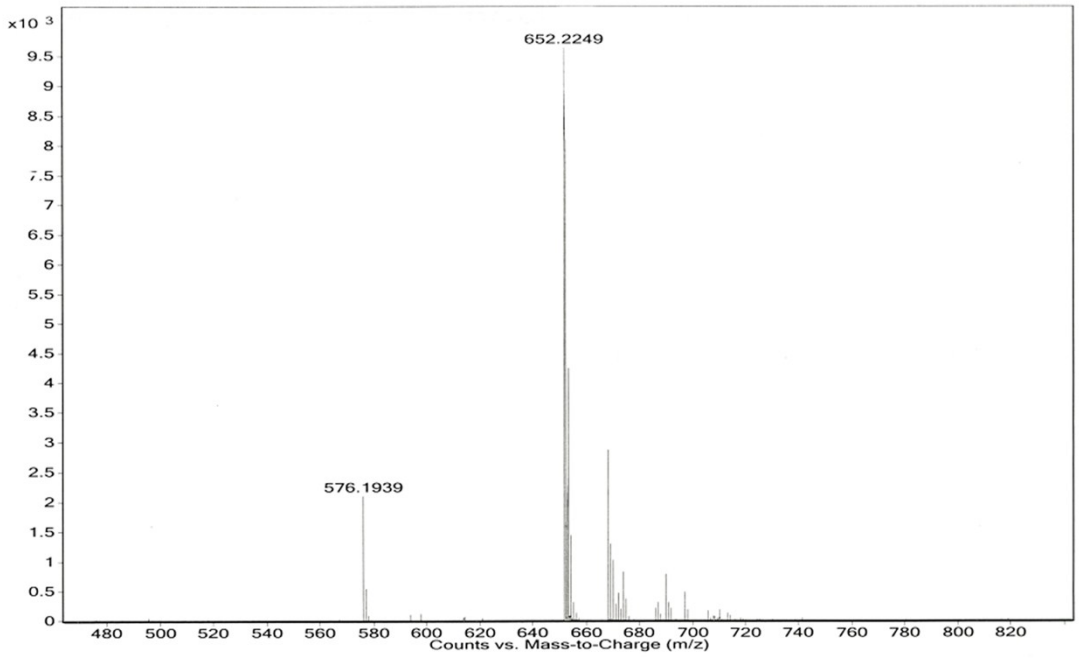

Fig. S2 High resolution mass spectrum of probe **1**.

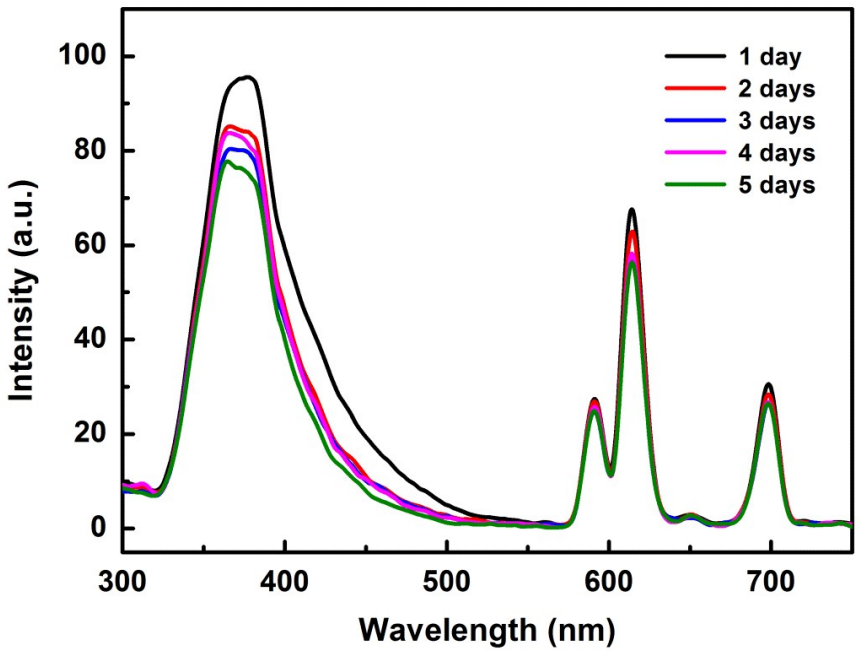

Fig. S3 Fluorescence emission spectra of **1** dispersed into water solutions as the suspensions within 5 days.

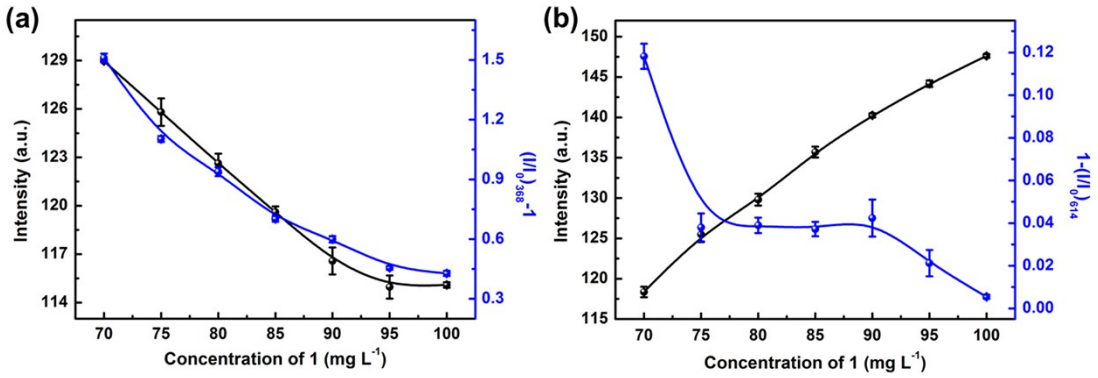

Fig. S4 (a) The effect of concentration of **1** on the fluorescence intensity and enhancing efficiency after addition of 10 μM Pi. (b) The effect of concentration of **1** on the fluorescence intensity and qunching efficiency after addition of 10 μM Pi.

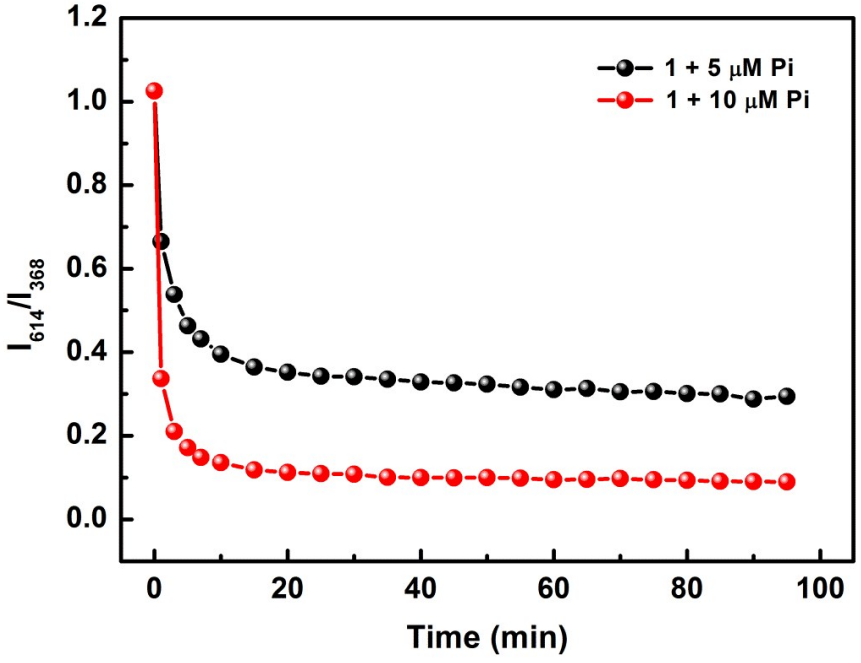

Fig. S5 Effect of reaction time of **1** on the fluorescence intensity ratio (I_{614}/I_{368}) in the presence of 5 μM (black) and 10 μM (red) Pi.

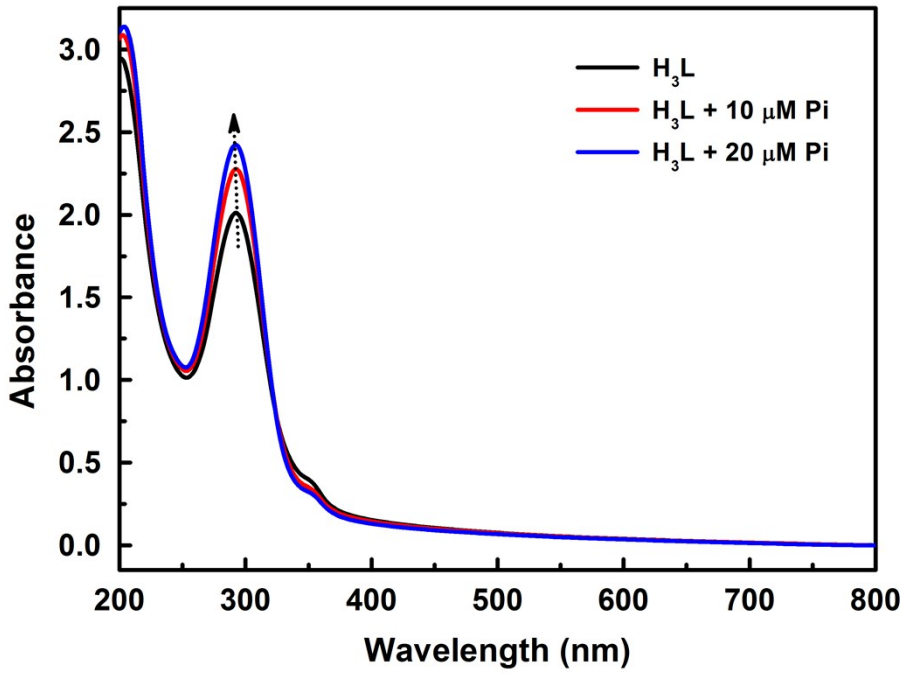

Fig. S6 UV-vis absorption spectra of free ligand H_3L and H_3L in the presence of various concentrations of Pi.

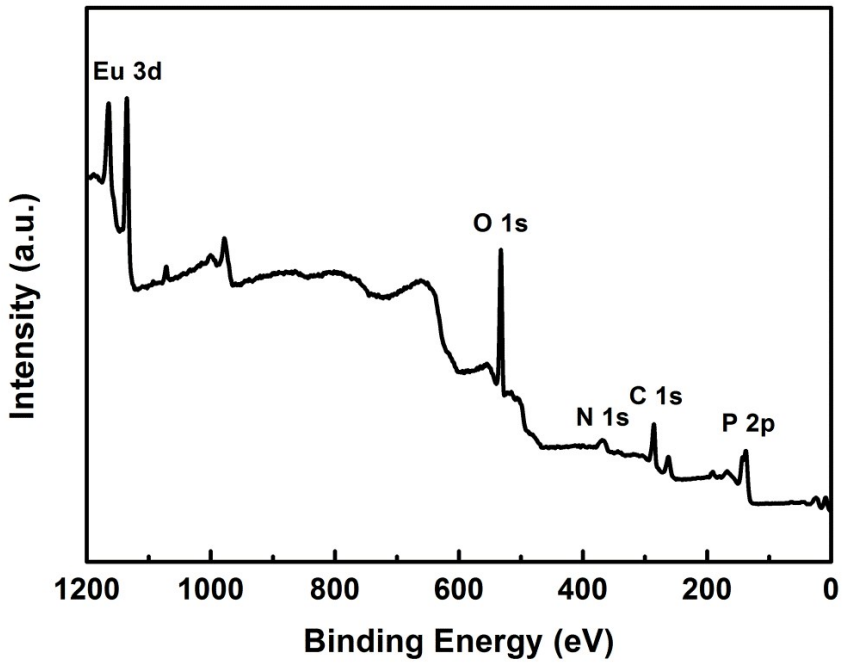

Fig. S7 Full-scan XPS spectrum of **1** after incubation with Pi.

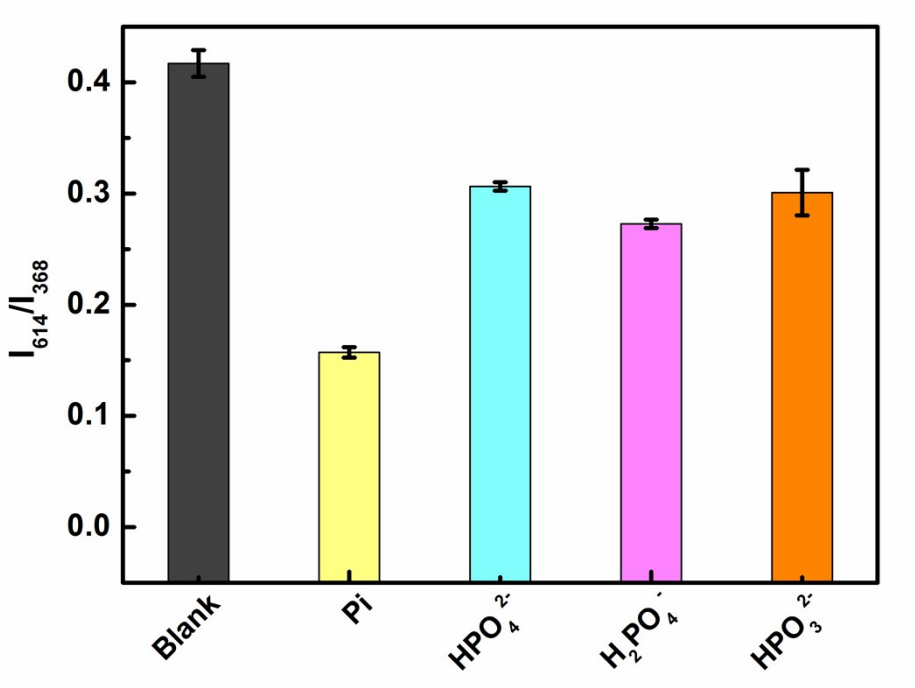

Fig. S8 Fluorescence intensity ratio (I_{614}/I_{368}) of **1** after addition of different phosphorus containing species.

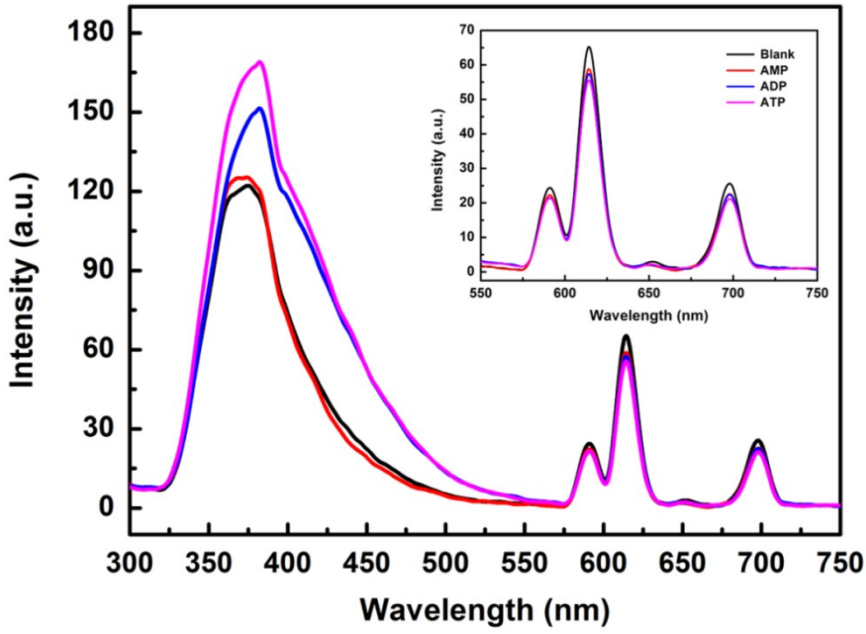

Fig. S9 Fluorescence emission spectra of **1** with 10 μM of AMP, ADP and ATP nucleoside phosphates added, respectively. Inset: The magnification of fluorescence emission spectra from 550-750 nm.

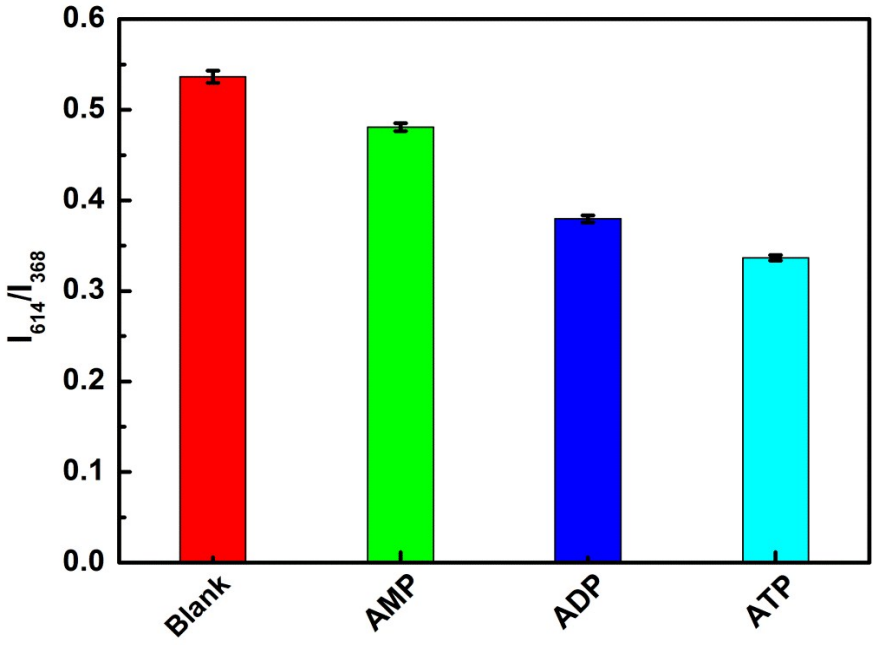

Fig. S10 Fluorescence intensity ratio (I_{614}/I_{368}) of **1** in the presence of 10 μM nucleoside phosphates including AMP, ADP and ATP.

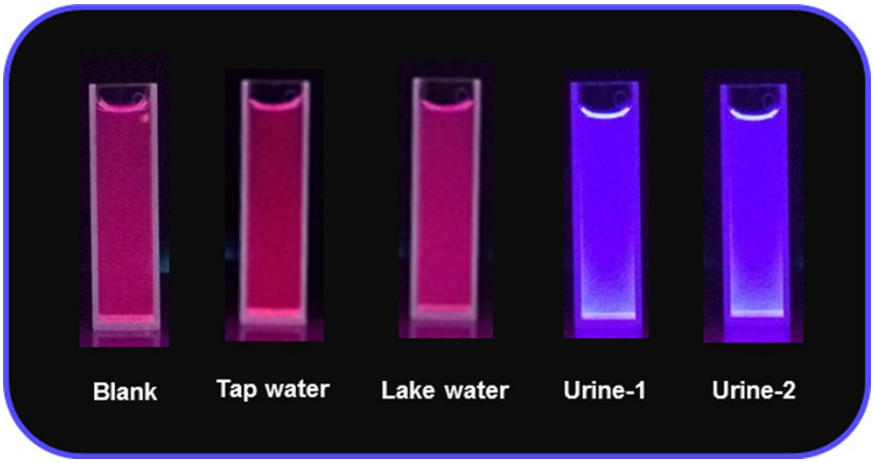

Fig. S11 Photographs of **1** with the addition of different original (undiluted) real samples under 302 nm UV light irradiation.

Table S1 Crystallographic data and details of refinements for **1**.[a,b]

Complex	**1**
Empirical formula	$C_{22.95}H_{16.25}EuN_{0.65}O_8$
Formula weight	581.09
Crystal system	Monoclinic
Space group	C_2/c
a /Å	33.0877(8)
b /Å	13.6008(4)
c /Å	14.1080(3)
α /°	90
β /°	102.249(2)
γ /°	90
V /Å^3	6204.3(3)
Z	8
D /g·cm^{-3}	1.231
μ /mm^{-1}	14.779
F(000)	2300
Crystal size /mm^3	0.25 × 0.22 × 0.20
θ range for data collection /°	9.136 - 147.26
Limiting indices	-31 <= h <= 40, -13 ≤ k ≤ 13, -14 ≤ l ≤ 17, -16 <= k <= 9, -17 <= l <= 15
Reflections collected / unique (R_{int}) unique (Rint)	12348 / 6102(0.0343)
Completeness	97.5%
Max. and min. transmission	0.062 and 0.052
Data / restraints / parameters	6102 / 82 / 312
Goodness-of-fit on F^2	1.043
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0399, wR_2 = 0.1019
R indices (all data)	R_1 = 0.0472, wR_2 = 0.1081 wR_2 = 0.2069
Largest diff. peak and hole /e·Å^{-3}	1.43 / -0.77

[a] $R_1 = \Sigma||F_o| - |F_c||/|F_o|$. [b] $\omega R_2 = [\Sigma w(|F_o|^2-|F_c^2|^2/w|F_o^2|^2]^{1/2}$.

Table S2 Selected bond lengths /Å and bond angles /° for complex **1**.

Eu(1)-O(1)	2.393(3)	Eu(1)-O(3)	2.447(3)
Eu(1)-O(4)	2.368(3)	Eu(1)-O(7)	2.461(4)
Eu(1)-O(2)	2.388(3)	Eu(1)-O(5)	2.531(3)
Eu(1)-O(6)	2.435(3)	Eu(1)-O(7)	2.461(4)
O(1)- Eu (1) -O(3)	72.78(12)	O(1)- Eu (1) -O(4)	68.85(9)
O(1)- Eu (1) -O(5)	70.65(11)	O(1)- Eu (1) -O(6)	80.19(12)
O(1)- Eu (1) -O(7)	137.54(14)	O(3)- Eu (1) -O(8)	135.5(2)
O(2)- Eu (1) -O(3)	91.58(11)	O(2)- Eu (1) -O(4)	67.86(9)
O(2)- Eu (1) -O(5)	142.70(11)	O(2)- Eu (1) -O(6)	142.01(13)
O(2)- Eu (1) -O(7)	71.48(12)	O(2)- Eu (1) -O(8)	75.9(2)
O(3)- Eu (1) -O(4)	50.53(9)	O(3)- Eu (1) -O(5)	125.36(10)
O(3)- Eu (1) -O(7)	73.24(15)	O(3)- Eu (1) -O(8)	143.5(6)
O(4)- Eu (1) -O(5)	82.65(10)	O(4)- Eu (1) -O(6)	133.78(11)
O(4)- Eu (1) -O(7)	147.06(12)	O(4)- Eu (1) -O(8)	81.9(4)
O(5)- Eu (1) -O(6)	52.32(11)	O(6)- Eu (1) -O(7)	70.91(13)
O(6)- Eu (1) -O(8)	91.6(7)	O(7)- Eu (1) -O(8)	76.0(4)

Table S3 Comparison of various methods for the determination of Pi.

Analytic methods	Systems	Linear range (μM)	Detection limit (μM)	Ref.
Colorimetric method	MA-AuNPs	0.5-30	0.076	[1]
Colorimetric method	Fe_3O_4 MNPs-TMB-H_2O_2	0.2-200	0.11	[2]
Electrochemical method	Al-Cu/Si-p/SiO_2/Si_3N_4/ Cu(II)Pc-PAA	0.0001-1	0.001	[3]
Electrochemical method	Three-electrode	1-20	0.3	[4]
Electrochemical method	Ni-BPE	40-1000	0.3	[5]
Fluorescent method Signal[a]	ZnO QDs-MOF-5 Fluorescence enhancing	0.5-12	0.053	[6]
Fluorescent method Signal	UiO-66-NH_2 Fluorescence enhancing	5-150	1.25	[7]
Fluorescent method Signal	Mn: ZnTe/ZnSe QDs Fluorescence quenching	0.67-50	0.2	[8]
Fluorescent method Signal	$\{[EuL(H_2O)_{1.35}(DMF)_{0.65}]\cdot 1.9DMF\}_n$ (**1**) Ratio fluorescence	0.1-15	0.052	This work

[a]Fluorescence signal changing mode.

Table S4 Analytical results (mean ± σ, n=3) for the detection of Pi in real samples.

Samples	Spiked (μM)	Measured (μM)	Recovery (%)	R.S.D. (n=3, %)
Tap water	0	3.83 ± 0.35		
	5	8.86 ± 0.04	100.6	1.7
Lake water	0	9.91 ± 0.01		
	5	14.55 ± 0.03	92.8	2.3
Urine-1[a]	0	10.06 ± 0.01		
	5	14.95 ± 0.13	97.8	4.3
Urine-2[a]	0	5.28 ± 0.01		
	5	10.25 ± 0.06	99.4	1.4

[a]Diluted urine sample.

Notes and references

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