

Electronic Supplementary Information (ESI) for

# **Tri-functional Fe-Zr bi-metal–organic frameworks enable high-performance phosphate ion ratiometric fluorescent detection**

Xin Li,<sup>a,b,c,#</sup> Peng Liu,<sup>a,#</sup> Xiangheng Niu,<sup>a,b,\*</sup> Kun Ye,<sup>a</sup> Liang Ni,<sup>a</sup> Dan Du,<sup>b</sup> Jianming Pan,<sup>a</sup> Yuehe Lin<sup>b,\*</sup>

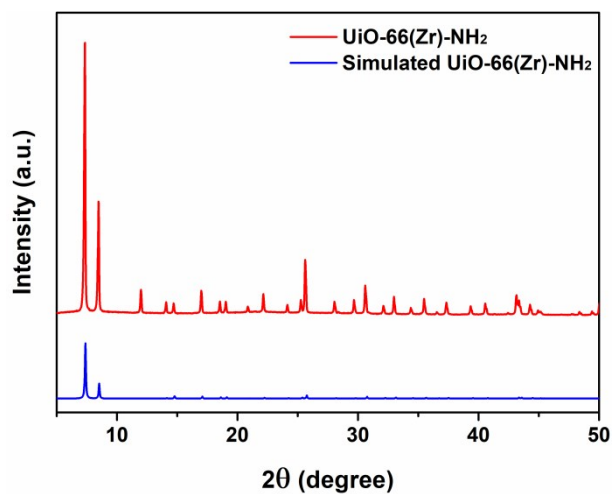
<sup>a</sup> Institute of Green Chemistry and Chemical Technology, School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, PR China

<sup>b</sup> School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164, USA

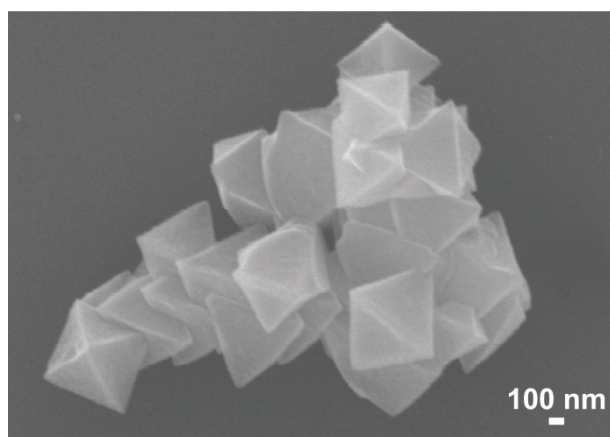
<sup>c</sup> School of Environment and Safety Engineering, Jiangsu University, Zhenjiang 212013, PR China

# Authors who contribute to the work equally

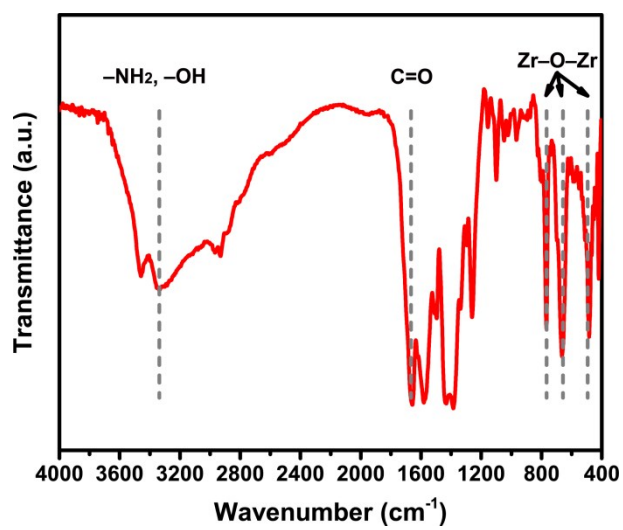
\* Corresponding authors. E-mail: niuxiangheng@ujs.edu.cn (X. Niu); yuehe.lin@wsu.edu (Y. Lin)



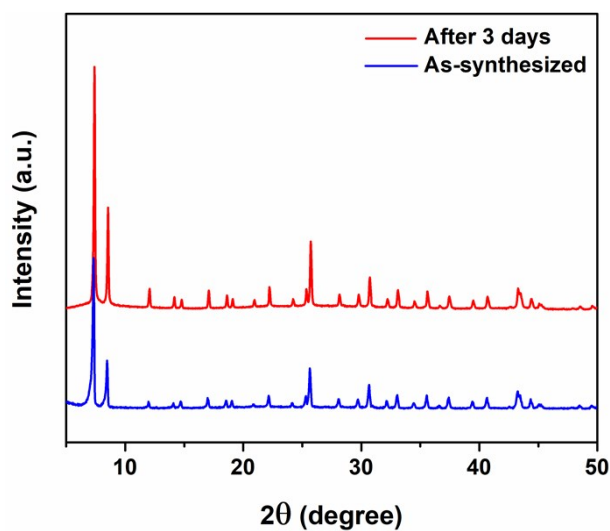
**Figure S1.** XRD pattern of UiO-66(Zr)-NH<sub>2</sub>.



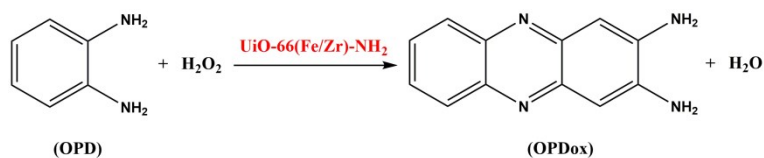
**Figure S2.** SEM image of UiO-66(Zr)-NH<sub>2</sub>.



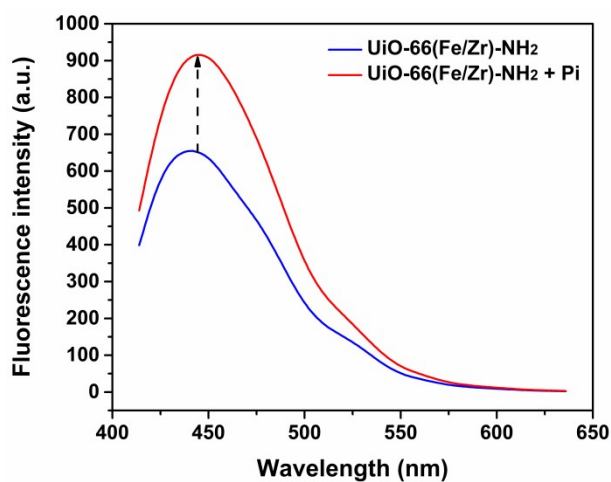
**Figure S3.** FTIR spectrum of UiO-66(Zr)-NH<sub>2</sub>.



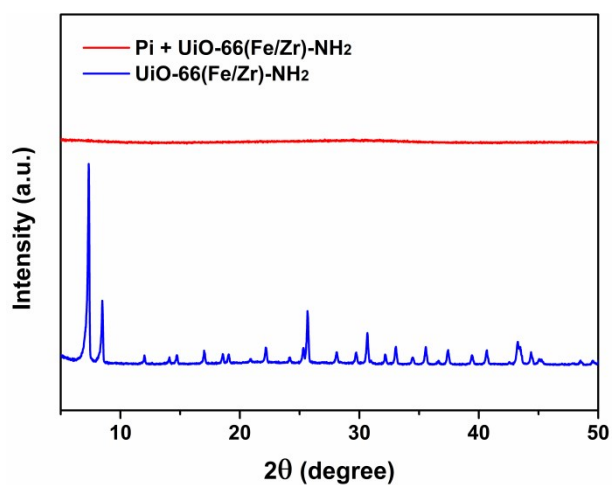
**Figure S4.** XRD pattern of UiO-66(Fe/Zr)-NH<sub>2</sub> after suspension in NaAc-HAc buffer (pH 4.0) for three days.



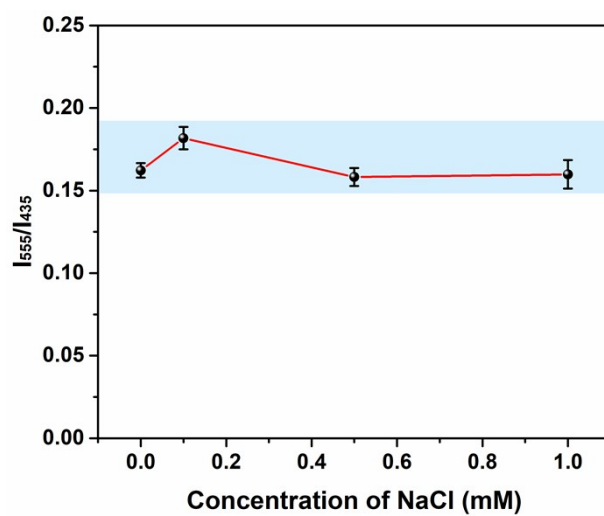
**Figure S5.** H<sub>2</sub>O<sub>2</sub>-assisted oxidation of OPD to OPDox under the peroxidase-mimetic catalysis of UiO-66(Fe/Zr)-NH<sub>2</sub>.



**Figure S6.** Impact of Pi on the intrinsic fluorescent property of UiO-66(Fe/Zr)-NH<sub>2</sub>.



**Figure S7.** XRD comparison of UiO-66(Fe/Zr)-NH<sub>2</sub> before and after Pi adsorption.



**Figure S8.** Influence of ionic strength on the I<sub>555</sub>/I<sub>435</sub> value of the UiO-66(Fe/Zr)-NH<sub>2</sub>+H<sub>2</sub>O<sub>2</sub>+OPD+Pi system (Pi concentration: 0.33 mM).

**Table S1.** Performance comparison of our sensing platform with other methods for Pi detection.

<b>Material</b>	<b>Function</b>	<b>Measurement method</b>	<b>Detection range (<math>\mu\text{M}</math>)</b>	<b>LOD (<math>\mu\text{M}</math>)</b>	<b>Ref.</b>
$\text{Fe}_3\text{O}_4$ MNPs	Peroxidase mimic	Colorimetric	0.2–200	0.11	[1]
UiO-66(Zr)- $\text{NH}_2$	Fluorescent label	Fluorescent	5–150	1.25	[2]
CBNPs	Electrode modifier	Electrochemical	Up to 80	6	[3]
GODs	Fluorescent label	Fluorescent	0.5–190	0.1	[4]
Mn-ZnS-QDs	Phosphorescent label	Phosphorescent	8–320	2.71	[5]
s-GQDs	Fluorescent label	Fluorescent	0.25–7.5	0.1	[6]
UiO-66(Fe/Zr)- $\text{NH}_2$	Recognition motif, fluorescent label, and peroxidase mimic	Ratiometric fluorescent	0.2–266.7	0.085	This work

**Table S2.** Results of our sensing platform for Pi determination in real samples.

Sample	Pi in original samples		Pi in spiked samples		Recovery rate (%)
	detected by our sensor ( $\mu\text{M}$ , N = 3)	Spiked ( $\mu\text{M}$ )	detected by our sensor ( $\mu\text{M}$ , N = 3)		
Drinking water	Not detected	33.3	34.6	103.9	
		133.3	136.2	102.2	
		200.0	203.9	102.0	
Tap water	Not detected	33.3	34.0	102.1	
		133.3	132.3	99.2	
		200.0	203.8	101.9	
River water 1#	Not detected	66.7	65.8	98.6	
		133.3	137.1	102.8	
		200.0	195.9	98.0	
River water 2#	19.4	66.7	86.7	100.9	
		100.0	116.6	97.2	
		133.3	157.1	103.3	
River water 3#	98.0	33.3	136.9	116.8	
		66.7	161.8	95.6	
		100.0	196.5	98.5	

## References

- [1] C.X. Chen, L.X. Lu, Y. Zheng, D. Zhao, F. Yang, X.R. Yang, A new colorimetric protocol for selective detection of phosphate based on the inhibition of peroxidase-like activity of magnetite nanoparticles, *Anal. Methods*, 7 (2015) 161-167.
- [2] J. Yang, Y. Dai, X.Y. Zhu, Z. Wang, Y.S. Li, Q.X. Zhuang, J.L. Shi, J.L. Gu, Metal-organic frameworks with inherent recognition sites for selective phosphate sensing through their coordination-induced fluorescence enhancement effect, *J. Mater. Chem. A*, 3 (2015) 7445-7452.
- [3] D. Talarico, S. Cinti, F. Arduini, A. Amine, D. Moscone, G. Palleschi, Phosphate detection through a cost-effective carbon black nanoparticle-modified screen-printed electrode embedded in a continuous flow system, *Environ. Sci. Technol.*, 49 (2015) 7934-7939.
- [4] J.M. Bai, L. Zhang, R.P. Liang, J.D. Qiu, Graphene quantum dots combined with europium ions as photoluminescent probes for phosphate sensing, *Chem. Eur. J.*, 19 (2013) 3822-3826.
- [5] J. Qin, D.X. Li, Y.M. Miao, G.Q. Yan, Detection of phosphate based on phosphorescence of Mn doped ZnS quantum dots combined with cerium(III), *RSC Adv.*, 7 (2017) 46657-46664.
- [6] B.B. Chen, R.S. Li, M.L. Liu, H.Y. Zou, H. Liu, C.Z. Huang, Highly selective detection of phosphate ion based on a single-layered graphene quantum dots- $\text{Al}^{3+}$  strategy, *Talanta*, 178 (2018) 172-177.