## **Supporting Information**

Zinc(II)-based coordination polymer encapsulated by  $Tb^{3+}$  as multiresponsive luminescent sensor for  $Ru^{3+}$ ,  $Fe^{3+}$ ,  $CrO_4^{2-}$ ,  $Cr_2O_7^{2-}$ 

## and $MnO_4^-$

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Fig. S1 FTIR pattern for Zn-CP.

polymer	Zn-CP		
CCDC	1882227 C2 42H2 29N0 %O0 29Zno 1		
Formula	4		
fw	69.40		
temp (K)	296(2)		
cryst syst	Tetragonal		
Space group	P4 <sub>3</sub> 2 <sub>1</sub> 2		
a(Å)	10.4340(10)		
b(Å)	10.4340(10)		
$c(\text{\AA})$	20.752(5)		
$\alpha = \beta = \gamma(^{\circ})$	90		
$V(A^3)$	2259.2(7)		
Ζ	28		
ho (Mg/m <sup>3</sup> )	1.428		
Abs coeff (mm <sup>-1</sup> )	1.120		
F (000)	992		
GOF	0.924		

Table S1 Crystal data and structure refinement information for Zn-CP

$R_1/wR_2 [I > 2\sigma(I)]$	0.0310/0.0687
$R_1/wR_2$ (all data)	0.0406/0.0730

Bond lengths (Å)				
Zn(1)-N(2)#1	2.089(2)	Zn(1)-N(2)#2	2.089(2)	
Zn(1)-N(1)#3	2.104(2)	Zn(1)-N(1)	2.104(2)	
Zn(1)-O(1)	2.390(2)	Zn(1)-O(1)#3	2.390(2)	
N(2)-Zn(1)#4	2.089(2)			
Bond angles (°)				
N(2)#1-Zn(1)-N(2)#2	96.22(14)	N(2)#1-Zn(1)-N(1)#3	142.64(9)	
N(2)#2-Zn(1)-N(1)#3	94.05(11)	N(2)#1-Zn(1)-N(1)	94.05(11)	
N(2)#2-Zn(1)-N(1)	142.64(9)	N(1)#3-Zn(1)-N(1)	99.21(14)	
N(2)#1-Zn(1)-O(1)	91.01(9)	N(2)#2-Zn(1)-O(1)	84.85(8)	
N(1)#3-Zn(1)-O(1)	125.70(9)	N(1)-Zn(1)-O(1)	59.10(8)	
N(2)#1-Zn(1)-O(1)#3	84.85(8)	N(2)#2-Zn(1)-O(1)#3	91.01(9)	
N(1)#3-Zn(1)-O(1)#3	59.10(8)	N(1)-Zn(1)-O(1)#3	125.69(9)	
O(1)-Zn(1)-O(1)#3	173.81(11)			

Table S2 Selected bond lengths (A°) and angles (°) for Zn-CP



Fig. S2 Thermogravimetric curve of Zn-CP.



**Fig. S3** PXRD patterns for Zn-CP: (a) simulated; (b) experimental; (c) 1 days after immersion in water; (d) 1 days after immersion in FeCl<sub>3</sub> solution (e) 1 days after immersion in CoCl<sub>2</sub> solution; (f) 1 days after immersion in NiCl<sub>2</sub>

solution; (g) 1 days after immersion in  $CuCl_2$  solution; (h) 12 h after immersion in  $CH_3OH$ ; (i) 12 h after immersion in  $C_2H_5OH$ ; (j) 12 h after immersion in acetone; (k) 12 h after immersion in  $CH_2Cl_2$ ; (l) 12 h after immersion in DMF. PXRD pattern calculated from the single-crystal structure.



**Fig. S4** PXRD patterns for Zn-CP at different temperatures,  $120^{\circ}$ C (red line);  $160^{\circ}$ C (green line);  $180^{\circ}$ C (blue line) and the simulated one calculated from the single crystal structure analysis (black line).



Fig. S5 PXRD patterns for Tb<sup>3+</sup>@Zn-CP: (a) simulated of Zn-CP; (b) experimental of Zn-CP; (c) experimental of

Tb<sup>3+</sup>@Zn-CP; (d) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in FeCl<sub>3</sub> solution; (e) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in RuCl<sub>3</sub> solution; (f) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in KMnO<sub>4</sub> solution; (g) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in K<sub>2</sub>CrO<sub>4</sub> solution; (h) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in K<sub>2</sub>CrO<sub>4</sub> solution; (h) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in K<sub>2</sub>CrO<sub>4</sub> solution; (h) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in K<sub>2</sub>CrO<sub>4</sub> solution; (h) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in K<sub>2</sub>CrO<sub>4</sub> solution; (h) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in K<sub>2</sub>CrO<sub>4</sub> solution; (h) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in K<sub>2</sub>CrO<sub>4</sub> solution; (h) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in K<sub>2</sub>CrO<sub>4</sub> solution; (h) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in K<sub>2</sub>CrO<sub>4</sub> solution; (h) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in K<sub>2</sub>CrO<sub>4</sub> solution; (h) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in K<sub>2</sub>CrO<sub>4</sub> solution; (h) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in K<sub>2</sub>CrO<sub>4</sub> solution; (h) experimental of Tb<sup>3+</sup>@Zn-CP 12 h after immersion in K<sub>2</sub>CrO<sub>4</sub> solution.

<b>Table S3</b> The detailed ICP studies of Tb <sup>3+</sup> @Zn-C	Ľ	p	)
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Sample	Zn(ppm)	Tb(ppm)	Mn(ppm)	Ru(ppm)	Cr(ppm)	Fe(ppm)
Tb <sup>3+</sup> @Zn-CP	1.312	0.0398				
Tb <sup>3+</sup> @Zn-CP+Fe <sup>3+</sup>	2.897	0.0239				0.1017
$Tb^{3+}@Zn-CP+Ru^{3+}$	1.093	Below detection limit		Below detection limit		
Tb <sup>3+</sup> @Zn-CP+MnO <sub>4</sub> -	2.354	0.0530	0.2275			
Tb <sup>3+</sup> @Zn-CP+CrO4 <sup>2-</sup>	2.747	0.0150			Below detection limit	
$Tb^{3+}@Zn-CP+Cr_2O_7^{2-}$	2.509	0.0171			Below	
detection limit/ ppm		0.007		0.003	detection limit 0.002	





Fig. S6 The XPS spectra of Zn-CP and Tb<sup>3+</sup>@Zn-CP samples: (a) the survey spectrum,

the high resolution XPS spectra of (b) Tb 3d, (c) Tb 4d, respectively.



**Fig. S7** liquid-state luminescent spectra of modbc ligand (blue), Zn-CP (green), Tb<sup>3+</sup>@Zn-CP (orange and navy) in 5 mM Tris-HCl/NaCl buffer (pH 7.0). slit width: 4 nm.



Fig. S8 Liquid-state luminescent spectra of Zn-CP upon excitation at about 312 nm (a) and Tb<sup>3+</sup>@Zn-CP upon excitation at about 330 nm (b) with different pH values (1.0~13.0) in H<sub>2</sub>O.



Fig. S9 Luminous intensity of Zn-CP upon different ions (Ru<sup>3+</sup>, Ag<sup>+</sup>, Cd<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Ca<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Fe<sup>2+</sup>, Hg<sup>2+</sup> and Fe<sup>3+</sup>) in 5 mM Tris-HCl/NaCl buffer (pH 7.0). [Zn-CP] = 10  $\mu$ M and [ions] = 50  $\mu$ M.  $\lambda_{ex}$ : 312 nm,  $\lambda_{F}$ : 395 nm, slit width: 4 nm.



**Fig. S10** Luminous intensity of Zn-CP upon different ions  $(SO_4^{2-}, PO_4^{3-}, CrO_4^{2-}, Cr_2O_7^{2-}, MnO_4^{-}, I^-, CO_3^{2-}, HCO_3^{-}, C_2O_4^{2-})$  in 5 mM Tris-HCl/NaCl buffer (pH 7.0). [Zn-CP] = 10  $\mu$ M and [ions] = 50  $\mu$ M.  $\lambda_{ex}$ : 312 nm,  $\lambda_F$ : 395 nm, slit width: 4 nm.



**Fig. S11** Luminescence quenching of Tb<sup>3+</sup>@Zn-CP in 5 mM Tris-HCl/NaCl buffer (pH 7.0) with gradual addition of 1 mM solution of Fe<sup>3+</sup>.  $\lambda_{ex}$ : 330 nm,  $\lambda_F$ : 390 nm, slit width: 4 nm. [Tb<sup>3+</sup>@Zn-CP] = 10  $\mu$ M.



**Fig. S12** Luminescence quenching of Tb<sup>3+</sup>@Zn-CP in 5 mM Tris-HCl/NaCl buffer (pH 7.0) with gradual addition of 1 mM solution of Ru<sup>3+</sup>.  $\lambda_{ex}$ : 330 nm,  $\lambda_F$ : 390 nm, slit width: 4 nm. [Tb<sup>3+</sup>@Zn-CP] = 10  $\mu$ M.



**Fig. S13** the Stern–Volmer plots of  $I_0/I$  versus [Fe<sup>3+</sup>] and [Ru<sup>3+</sup>], respectively (insets: the related Stern–Volmer plots at low [Fe<sup>3+</sup>] and [Ru<sup>3+</sup>].  $\lambda_{ex}$ : 330 nm,  $\lambda_F$ : 390 nm, slit width: 4 nm. [Tb<sup>3+</sup>@Zn-CP] = 10  $\mu$ M.

S. No	Probe	LOD (M)	Ref
1	{[Cd(L)-(BPDC)]·2H <sub>2</sub> O}n probe	2.21 ×10 <sup>-6</sup> for Fe <sup>3+</sup>	S1
	$\{[Cd(L)(SDBA)(H_2O)] \cdot 0.5H_2O\}n \text{ probe}$	$7.14 \times 10^{-6}$ for Fe <sup>3+</sup>	
2	Zn-L-MOF probe	$6.4 \times 10^{-6}$ for Fe <sup>3+</sup>	S2
3	Zn(II)-based MOF probe	$2 \times 10^{-6}$ for Fe <sup>3+</sup>	<b>S</b> 3
4	Ru probe	5.03 nm means	S4
		0.51 ppb for Ru <sup>3+</sup>	
5	Europium-Based MOF probe	0.793× 10 <sup>-6</sup> for	S5
		Fe <sup>3+</sup>	
6	${[Eu(Hdcppa)(H_2O)_2] \cdot H_2O}n$ probe	10 <sup>-6</sup> for Fe <sup>3+</sup>	S6
7	Tb <sup>3+</sup> @Cd-P probe	$6.6 \times 10^{-7}$ for Fe <sup>3+</sup>	S7
8	Cd-P probe	$4.7 \times 10^{-8}$ for Fe <sup>3+</sup>	S7
9	[Zn(modbc) <sub>2</sub> ]n	$0.57 \times 10^{-6}$ for Fe <sup>3+</sup>	This work
10	[Zn(modbc) <sub>2</sub> ]n	0.27× 10 <sup>-6</sup> for	This work
		Ru <sup>3+</sup>	

Table S4. Comparison of the probes with literature reports for sensing Fe<sup>3+</sup>, Ru<sup>3+</sup>.

S1. S. G. Chen, Z. Z. Shi, L. Qin, H. L. Jia, H. G. Zheng, Two New Luminescent Cd(II)-Metal–Organic Frameworks as Bifunctional Chemosensors for Detection of Cations  $Fe^{3+}$ , Anions  $CrO_4^{2-}$ , and  $Cr_2O_7^{2-}$  in Aqueous Solution, *Cryst. Growth Des.* 2017, **17**, 67–72.

S2. Yu, C. Y.; Sun, X. D.; Zou, L. F.; Li, G. H.; Zhang, L. R.; Liu, Y. L. A Pillar-Layered Zn-LMOF with Uncoordinated Carboxylic Acid Sites: High Performance for Luminescence Sensing Fe<sup>3+</sup> and TNP. *Inorg. Chem.* 

S3. Lv, R.; Li, H.; Su, J.; Fu, X.; Yang, B. Y.; Gu, W.; Liu, X. Zinc Metal–Organic Framework for Selective Detection and Differentiation of Fe(III) and Cr(VI) Ions in Aqueous Solution. *Inorg. Chem.* 2017, *56*, 12348–12356.

S4. B. Chen, F. L. Song, S. G. Sun, J. L.i Fan, X. J. Peng, A Highly Sensitive Fluorescent Chemosensor for Ruthenium: Oxidation Plays a Triple Role, *Chem. Eur. J.* 2013, **19**, 10115–10118.

S5. Purna, C. R.; Mandal, S. Europium-Based Metal–Organic Framework as a Dual Luminescence Sensor for the Selective Detection of the Phosphate Anion and Fe<sup>3+</sup> Ion in Aqueous Media. *Inorg. Chem.* **2018**, *57*, 11855–11858

S6. Zhang, H. J.; Fan, R. Q.; Chen, W.; Fan, J. Z.; Dong, Y. W.; Song, Y.; Du, X.; Wang, P.; Yang, Y. L. 3D Lanthanide Metal–Organic Frameworks Based on Mono-, Tri-, and Heterometallic Tetranuclear Clusters as Highly Selective and Sensitive Luminescent Sensor for Fe<sup>3+</sup> and Cu<sup>2+</sup> Ions. *Cryst. Growth Des.* **2016**, *16*, 5429–5440.

S7 Y. D. Wu, M. H. Lin, D. Y. Liu, M. Liu, J. Qian, Two-dimensional Cd(II) coordination polymer encapsulated by Tb<sup>3+</sup> as a reversible luminescent probe for Fe<sup>3+</sup>. *RSC Adv.*, **2019**, *9*, 34949–34957.



Fig. S14 The relative fluorescence intensity of a 10  $\mu$ M solution of Tb<sup>3+</sup>@ Zn-CP upon addition of 1.0 and 9.0 equiv of Fe<sup>3+</sup> in the presence of 9.0 equiv of background ions (M<sup>n+</sup>).  $\lambda_{ex}$ : 330 nm,  $\lambda_{F}$ : 390 nm, slit width: 4 nm.



Fig. S15 The relative fluorescence intensity of a 10  $\mu$ M solution of Tb<sup>3+</sup>@ Zn-CP upon addition of 1.0 and 9.0 equiv of Ru<sup>3+</sup> in the presence of 9.0 equiv of background ions (M<sup>n+</sup>).  $\lambda_{ex}$ : 330 nm,  $\lambda_F$ : 390 nm, slit width: 4 nm.



**Fig. S16** The variation of luminescent intensity of Tb<sup>3+</sup>@ Zn-CP at 390 nm with immersion time in 24 μM RuCl<sub>3</sub> aqueous solution (blue, a); with immersion time in 24 μM Fe(NO<sub>3</sub>)<sub>3</sub> aqueous solution (olive, b).



**Fig. S17** Luminescence quenching of Tb<sup>3+</sup>@Zn-CP in 5 mM Tris-HCl/NaCl buffer (pH 6.0) with gradual addition of 1 mM solution of  $Cr_2O_7^{2-}$ .  $\lambda_{ex}$ : 330 nm,  $\lambda_F$ : 390 nm, slit width: 4 nm. [Tb<sup>3+</sup>@Zn-CP] = 10  $\mu$ M.



**Fig. S18** Luminescence quenching of Tb<sup>3+</sup>@Zn-CP in 5 mM Tris-HCl/NaCl buffer (pH 8.0) with gradual addition of 1 mM solution of  $CrO_4^{2-}$ .  $\lambda_{ex}$ : 330 nm,  $\lambda_F$ : 390 nm, slit width: 4 nm. [Tb<sup>3+</sup>@Zn-CP] = 10  $\mu$ M.



**Fig. S19** Luminescence quenching of Tb<sup>3+</sup>@Zn-CP in 5 mM Tris-HCl/NaCl buffer (pH 7.0) with gradual addition of 1 mM solution of  $MnO_4^-$ .  $\lambda_{ex}$ : 330 nm,  $\lambda_F$ : 390 nm, slit width: 4 nm. [Tb<sup>3+</sup>@Zn-CP] = 10  $\mu$ M.



**Fig. S20** the Stern–Volmer plots of  $I_0/I$  versus  $Cr_2O_7^{2-}$ ,  $CrO_4^{2-}$  and  $MnO_4^-$  ion concentrations, respectively (insets: the related Stern–Volmer plots at low  $[Cr_2O_7^{2-}]$ ,  $[CrO_4^{2-}]$  and  $[MnO_4^-]$ .  $\lambda_{ex}$ : 330 nm,  $\lambda_F$ : 390 nm, slit width: 4 nm.  $[Tb^{3+}@Zn-CP] = 10 \ \mu\text{M}.$ 

S. No	Probe	LOD	Ref
1	$[H_2N(CH_3)_2]_2[Zn_2L(HPO_3)_2] \text{ probe}$	$1.09 \times 10^{-6} \mathrm{M}$ for	S1
		$Cr_2O_7^{2-}$	
2	${[Cd(L)-(BPDC)] \cdot 2H_2O}n \text{ probe}$	3.76×10 <sup>-5</sup> M for	S2
	${[Cd(L)(SDBA)(H_2O)] \cdot 0.5H_2O}n$ probe	$Cr_2O_7^{2-}$	
		$4.86 \times 10^{-5}$ M for	
		$CrO_4^{2-}$	
3	$[Cd_{3}{Ir(ppy-COO)_{3}}_{2}(DMF)_{2}(H_{2}O)_{4}] \cdot 6$	145.1 ppb for	S3
	$H_2O \cdot 2DMF$ probe	$Cr_2O_7^{2-}$	
4	[Tb <sub>2</sub> Ni <sub>3</sub> (HCAM) <sub>6</sub> (H <sub>2</sub> O) <sub>12</sub> ] n probe	$0.29 \times 10^{-6} \mathrm{M}$ for	S4
		$MnO_4^-$	
5	$\{[Ba_{3}La_{0.5}(\mu_{3}\text{-}L)_{2.5}(H_{2}O)_{3}(DMF)] \cdot (3DMF)\} n$	$0.28 \times 10^{-6} \mathrm{M}$ for	S5
	probe	$MnO_4^-$	
6	[Zn(modbc) <sub>2</sub> ]n	0.43× 10 <sup>-6</sup> M for	This work
		$Cr_2O_7^{2-}$	
7	[Zn(modbc) <sub>2</sub> ]n	0.10× 10 <sup>-6</sup> M for	This work
		CrO4 <sup>2-</sup>	
8	[Zn(modbc) <sub>2</sub> ]n	0.15× 10 <sup>-6</sup> M for	This work
		$MnO_4^-$	

**Table S5.** Comparison of the probes with literature reports for sensing  $Cr_2O_7^{2-}$ ,  $CrO_4^{2-}$  and  $MnO_4^{-}$ .

S1. Si-Fu Tang, Xiaomin Hou, A Highly Stable Dual Functional Zinc Phosphite Carboxylate as

Luminescent Sensor of Fe<sup>3+</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, Cryst. Growth Des. 2019, **19**, 45–48.

S2. S. G. Chen, Z. Z. Shi, L. Qin, H. L. Jia, H. G. Zheng, Two New Luminescent Cd(II)-Metal–Organic Frameworks as Bifunctional Chemosensors for Detection of Cations  $Fe^{3+}$ , Anions  $CrO_4^{2-}$ , and  $Cr_2O_7^{2-}$  in Aqueous Solution, *Cryst. Growth Des.* 2017, **17**, 67–72.

S3. Kun Fan, Song-Song Bao, Wei-Xuan Nie, Chwen-Haw Liao, and Li-Min Zheng, Iridium(III)-Based Metal–Organic Frameworks as Multiresponsive Luminescent Sensors for  $Fe^{3+}$ ,  $Cr_2O_7^{2-}$ , and  $ATP^{2-}$  in Aqueous Media, Inorg. Chem. 2018, 57, 1079–1089.

S4. Jing Qian, Mei-Mei Sun, Ming Liu, Wen Gu, Macromolecular Probe Based on a Ni II /Tb III Coordination Polymer for Sensitive Recognition of Human Serum Albumin (HSA) and MnO<sub>4</sub><sup>-</sup>, ACS Omega 2019, 4, 11949–11959.

S5. Ding, B.; Liu, S. X.; Cheng, Y.; Guo, C.; Wu, X. X.; Guo, J. H.; Liu, Y. Y.; Li, Y. Heterometallic Alkaline Earth-Lanthanide Ba(II)-La(III) Microporous Metal-Organic Framework as Bifunctional Luminescent Probes of

Al  $^{3+}$  and MnO<sub>4</sub><sup>-</sup>. Inorg. Chem. 2016, 55, 4391–4402.



Fig. S21 The relative fluorescence intensity of a 10  $\mu$ M solution of Tb<sup>3+</sup>@ Zn-CP upon addition of 1.0 and 6.0 equiv of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> in the presence of 6.0 equiv of background ions (M<sup>n+</sup>).  $\lambda_{ex}$ : 330 nm,  $\lambda_{F}$ : 390 nm, slit width: 4 nm.



Fig. S22 The relative fluorescence intensity of a 10  $\mu$ M solution of Tb<sup>3+</sup>@ Zn-CP upon addition of 1.0 and 6.0 equiv of CrO<sub>4</sub><sup>2-</sup> in the presence of 6.0 equiv of background ions (M<sup>n+</sup>).  $\lambda_{ex}$ : 330 nm,  $\lambda_F$ : 390 nm, slit width: 4 nm.



Fig. S23 The relative fluorescence intensity of a 10  $\mu$ M solution of Tb<sup>3+</sup>@ Zn-CP upon addition of 1.0 and 6.0 equiv of MnO<sub>4</sub><sup>-</sup> in the presence of 6.0 equiv of background ions (M<sup>n+</sup>).  $\lambda_{ex}$ : 330 nm,  $\lambda_F$ : 390 nm, slit width: 4 nm.





Fig. S24 The variation of luminescent intensity of Tb<sup>3+</sup>@ Zn-CP at 390 nm with immersion time in 24  $\mu$ M Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> aqueous solution (a); with immersion time in 24  $\mu$ M CrO<sub>4</sub><sup>2-</sup> aqueous solution (b); with immersion time in 24  $\mu$ M MnO<sub>4</sub><sup>-</sup> aqueous solution (c).



**Fig. S25** Color of Tb<sup>3+</sup>@Zn-CP dipped in KMnO<sub>4</sub>, K<sub>2</sub>CrO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, FeCl<sub>3</sub>, RuCl<sub>3</sub> solution by normal light and UV lamp.



Fig. S26 The XPS spectra of Tb<sup>3+</sup>@Zn-CP+MnO<sub>4</sub><sup>-</sup> samples: the survey spectrum and the high resolution XPS

spectra of Mn 2p.



Fig. S27 The high resolution XPS spectra of O 1s of Zn-CP, Tb<sup>3+</sup>@Zn-CP, Tb<sup>3+</sup>@Zn-CP+Ru<sup>3+</sup>, Tb<sup>3+</sup>@Zn-

 $CP + Fe^{3+}, \ Tb^{3+} @Zn - CP + Cr_2O_7{}^{2-}, \ Tb^{3+} @Zn - CP + CrO_4{}^{2-} \ and \ Tb^{3+} @Zn - CP + MnO_4{}^{-} \ samples.$ 



**Fig. S28** UV–vis absorption spectra of Tb<sup>3+</sup>@Zn-CP with different concentration of  $MnO_4^-$ . Solvent: DMF/H<sub>2</sub>O (3/1, v/v), c: 10  $\mu$ M for Tb<sup>3+</sup>@Zn-CP, from bottom to top, the equiv of  $MnO_4^-$ : 0, 5, 10, 15, 20, 25, 30.



Fig. S29 UV spectra of Fe<sup>3+</sup>, Ru<sup>3+</sup>, CrO<sub>4</sub><sup>2-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, MnO<sub>4</sub><sup>-</sup> in H<sub>2</sub>O; and Zn-CP, Tb<sup>3+</sup>@Zn-CP in DMF.



Fig. S30 The XPS spectra of  $Tb^{3+}$ @Zn-CP+  $Cr_2O_7^{2-}$  samples: the survey spectrum and the high resolution XPS



Fig. S31 The XPS spectra of Tb<sup>3+</sup>@Zn-CP+ CrO4<sup>2-</sup> samples: the survey spectrum and the high resolution XPS

spectra of Cr 2p.

spectra of Cr 2p.



**Fig. S32** UV–vis absorption spectra of Tb<sup>3+</sup>@Zn-CP with different concentration of  $Cr_2O_7^{2-}$ . Solvent: DMF/H<sub>2</sub>O (3/1, v/v), c: 10  $\mu$ M for Tb<sup>3+</sup>@Zn-CP, from bottom to top, the equiv of  $Cr_2O_7^{2-}$ : 0, 5, 10, 15, 20, 25, 30.



**Fig. S33** UV–vis absorption spectra of Tb<sup>3+</sup>@Zn-CP with different concentration of  $CrO_4^{2-}$ . Solvent: DMF/H<sub>2</sub>O (3/1, v/v), c: 10  $\mu$ M for Tb<sup>3+</sup>@Zn-CP, from bottom to top, the equiv of  $CrO_4^{2-}$ : 0, 1, 2, 3, 4, 5,

6.



Fig. S34 The XPS spectra of Tb<sup>3+</sup>@Zn-CP+Fe<sup>3+</sup> samples: the survey spectrum and the high resolution XPS spectra

of Fe 2p.



**Fig. S35** UV–vis absorption spectra of Tb<sup>3+</sup>@Zn-CP with different concentration of Fe<sup>3+</sup>. Solvent: DMF/H<sub>2</sub>O (3/1, v/v), c: 10  $\mu$ M for Tb<sup>3+</sup>@Zn-CP, from bottom to top, the equiv of Fe<sup>3+</sup>: 0, 1, 2, 3, 4, 5,6.



Fig. S36 The XPS spectra of Tb<sup>3+</sup>@Zn-CP+Ru<sup>3+</sup> samples: the survey spectrum and the high resolution XPS



Fig. S37 UV–vis absorption spectra of Tb<sup>3+</sup>@Zn-CP with different concentration of Ru<sup>3+</sup>. Solvent: DMF/H<sub>2</sub>O (3/1, v/v), c: 10  $\mu$ M for Tb<sup>3+</sup>@Zn-CP, from bottom to top, the equiv of Ru<sup>3+</sup>: 0, 1, 2, 3, 4, 5,

spectra of Ru 3d.



**Fig. S38** Temporal fluorescence decay of 10  $\mu$ M Zn-CP with 50  $\mu$ M Fe<sup>3+</sup>, Ru<sup>3+</sup>, CrO<sub>4</sub><sup>2-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, MnO<sub>4</sub><sup>-</sup> in 5 mM Tris-HCl/NaCl buffer (pH 7.0) excited at 330 nm and monitored at 390 nm; The data are obtained at 54.9 ps per point.

Table S6 Comparison of lifetimes of Tb<sup>3+</sup>@Zn-CP, Tb<sup>3+</sup>@Zn-CP+Fe<sup>3+</sup>, Tb<sup>3+</sup>@Zn-CP+Ru<sup>3+</sup>,

Compounds	$\tau_1(ns)$	B <sub>1</sub> (%)	$\tau_2(ns)$	B <sub>2</sub> (%)	τ(ns)
Zn-CP	47.28	2.25	2.15	97.75	3.17
Tb <sup>3+</sup> @Zn-CP	0.51	88.21	2.87	11.79	0.79
Tb <sup>3+</sup> @Zn-CP+Fe <sup>3+</sup>	0.48	87.09	2.69	12.91	0.77
Tb <sup>3+</sup> @Zn-CP+Ru <sup>3+</sup>	0.46	84.49	2.69	15.51	0.81
Tb <sup>3+</sup> @Zn-CP+MnO <sub>4</sub> -	0.48	84.76	2.76	15.24	0.83
Tb <sup>3+</sup> @Zn-CP+CrO <sub>4</sub> <sup>2-</sup>	2.86	10.91	0.50	89.09	0.76
$Tb^{3+} @Zn-CP+Cr_2O_7^{2-}$	0.48	84.58	2.59	15.42	0.81

 $Tb^{3+} @Zn-CP+Cr_2O_7{}^{2-}, Tb^{3+} @Zn-CP+CrO_4{}^{2-} and \ Tb^{3+} @Zn-CP+MnO_4{}^{-}.$