Electronic Supplementary Information (ESI)

Multi-responsive luminescent sensor based on a stable Eu(III) metal-organic framework for sensing Fe^{3+}, MnO_4^-, and $Cr_2O_7^{2-}$ in aqueous solution

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Table S1. Selected bond lengths (Å) and angles (°) for **JXUST-9**.

Eu1—O8	2.353(8)	Eu1—O1^{ii}	2.485(8)
Eu1—O4	2.392(7)	Eu1—N2	2.558(14)
Eu2—O7^{iv}	2.323(9)	Eu2—N3^{v}	2.450(13)
Eu2—O6^{v}	2.363(8)	Eu2—O4^{vi}	2.509(8)
Eu2—O9	2.377(9)	Eu2—O3^{vi}	2.541(9)
Eu2—O1W	2.411(9)	Eu2—O1	2.872(8)
Eu2—O2	2.444(8)		
O8—Eu1—O8^{i}	145.7(5)	O1^{ii}—Eu1—O1^{iii}	80.5(4)
O8—Eu1—O4	94.3(3)	O8—Eu1—N2	70.3(4)
O8^{i}—Eu1—O4	96.7(3)	O8^{i}—Eu1—N2	143.8(4)
O4—Eu1—O4^{i}	142.2(4)	O4—Eu1—N2	69.2(4)
O8—Eu1—O1^{ii}	80.6(3)	O4^{i}—Eu1—N2	80.7(4)
O8^{i}—Eu1—O1^{ii}	73.4(3)	O1^{ii}—Eu1—N2	134.6(4)
O4—Eu1—O1^{ii}	149.0 (3)	O1^{iii}—Eu1—N2	120.8(4)
O4^{i}—Eu1—O1^{ii}	68.8(3)	N2—Eu1—N2^{i}	74.6(5)
O7^{iv}—Eu2—O6^{v}	78.1(3)	O1W—Eu2—O4^{vi}	127.8(3)
O7^{iv}—Eu2—O9	87.0(4)	O2—Eu2—O4^{vi}	82.0(3)
O6^{v}—Eu2—O9	73.4(4)	N3^{v}—Eu2—O4^{vi}	131.6(4)
O7^{iv}—Eu2—O1W	78.3(4)	O7^{iv}—Eu2—O3^{vi}	126.7(3)
O6^{v}—Eu2—O1W	71.1(4)	O6^{v}—Eu2—O3^{vi}	133.0(3)
O9—Eu2—O1W	143.9(4)	O9—Eu2—O3^{vi}	69.7(4)
O7^{iv}—Eu2—O2	124.1(3)	O1W—Eu2—O3^{vi}	143.9(4)
O6^{v}—Eu2—O2	133.3(3)	O2—Eu2—O3^{vi}	70.2(3)
O9—Eu2—O2	139.2(4)	N3^{v}—Eu2—O3^{vi}	80.1(4)
O1W—Eu2—O2	74.2(4)	O4^{vi}—Eu2—O3^{vi}	51.7(3)
O7^{iv}—Eu2—N3^{v}	148.1(4)	O7^{iv}—Eu2—O1	76.5(3)
O6^{v}—Eu2—N3^{v}	70.2(4)	O6^{v}—Eu2—O1	135.7(3)
O9—Eu2—N3^{v}	87.7(5)	O9—Eu2—O1	139.7(3)
O1W—Eu2—N3^{v}	87.8(5)	O1W—Eu2—O1	68.3(3)
O2—Eu2—N3^{v}	78.0(4)	O2—Eu2—O1	48.3(3)
O7^{iv}—Eu2—O4^{vi}	78.0(3)	N3^{v}—Eu2—O1	124.7(4)
O6^{v}—Eu2—O4^{vi}	144.6(3)	O4^{vi}—Eu2—O1	61.2(2)
O9—Eu2—O4^{vi}	79.6(3)	O3^{vi}—Eu2—O1	91.1(3)

Symmetry codes: (i) -*x*+1, *y*, -*z*-3/2; (ii) *x*+1/2, *y*+1/2, *z*; (iii) -*x*+1/2, *y*+1/2, -*z*-3/2; (iv) *x*-1/2, *y*-1/2, *z*; (v) *x*, -*y*-1, -*z*-1; (vi) -*x*+1/2, *y*-1/2, -*z*-3/2; (vii) *x*, -*y*-2, -*z*-1.

Table S2. SHAPE analysis of the Eu^{III} ions in **JXUST-9**.

ions	label	shape	symmetry	distortion(τ)
Eu1	OP-8	Octagon	D_{8h}	30.854
	HPY-8	Heptagonal pyramid	C_{7v}	23.235
	HBPY-8	Hexagonal bipyramid	D_{6h}	16.015
	CU-8	Cube	O_h	8.617
	SAPR-8	Square antiprism	D_{4d}	2.540
	TDD-8	Triangular dodecahedron	D_{2d}	**0.509**
	JGBF-8	Johnson gyrobifastigium J26	D_{2d}	13.902
	JETBPY-8	Johnson elongated triangular bipyramid J14	D_{3h}	30.532
	JBTPR-8	Biaugmented trigonal prism J50	C_{2v}	2.935
	BTPR-8	Biaugmented trigonal prism	C_{2v}	2.764
	JSD-8	Snub diphenoid J84	D_{2d}	2.574
	TT-8	Triakis tetrahedron	T_d	8.981
	ETBPY-8	Elongated trigonal bipyramid	D_{3h}	23.188
Eu2	EP-9	Enneagon	D_{9h}	33.061
	OPY-9	Octagonal pyramid	C_{8v}	22.381
	HBPY-9	Heptagonal bipyramid	D_{7h}	18.907
	JTC-9	Johnson triangular cupola J3	C_{3v}	15.231
	JCCU-9	Capped cube J8	C_{4v}	9.744
	CCU-9	Spherical-relaxed capped cube	C_{4v}	8.413
	JCSAPR-9	Capped square antiprism J10	C_{4v}	2.776
	CSAPR-9	Spherical capped square antiprism	C_{4v}	1.501
	JTCTPR-9	Tricapped trigonal prism J51	D_{3h}	2.978
	TCTPR-9	Spherical tricapped trigonal prism	D_{3h}	2.834
	JTDIC-9	Tridiminished icosahedron J63	C_{3v}	13.431
	HH-9	Hula-hoop	C_{2v}	10.365
	MFF-9	Muffin	C_s	**1.173**

Table S3. Comparison of the sensitivities of **JXUST-9** with previously reported MOFs to Fe^{3+}, MnO_4^- and $Cr_2O_7^{2-}$.

analytes	MOFs	solvents	detection limits (M)	references
Fe^{3+}	**JXUST-9**	H_2O	9.40×10^{-7}	This work
	$[Eu(L1)(H_2O)]\cdot 1.5H_2O$	H_2O	8.70×10^{-7}	1
	$\{[Zn_3(L2)(OH)(H_2O)_5]\cdot NMP\cdot 2H_2O\}_n$	H_2O	1.41×10^{-6}	2
	$\{Eu(L3)(H_2O)(DMA)\}_n$	H_2O	7.70×10^{-5}	3
	$[Eu(L4)(DMF)(H_2O)(HCOO)]_n$	DMAc	1.93×10^{-6}	4
	$\{[Zn_2(L6)(L5)]\cdot H_2O\}_n$	H_2O	6.19×10^{-6}	5
MnO_4^-	**JXUST-9**	H_2O	1.23×10^{-6}	This work
	$\{[Eu_3(L7)_3(HCOO)(OH)_2(DMF)]\cdot 3DMF\cdot 2H_2O\}_n$	H_2O	1.00×10^{-7}	6
	$\{[Zn_3(L2)(OH)(H_2O)_5]\cdot NMP\cdot 2H_2O\}_n$	H_2O	3.08×10^{-4}	2
	$[Eu(L4)(DMF)(H_2O)(HCOO)]_n$	H_2O	1.08×10^{-5}	4
	$\{Tb(L8)_{1.5}(H_2O)_{4.5}]_n$	H_2O	3.90×10^{-7}	7
	$[Cd(L9)(L10)]\cdot H_2O$	H_2O	2.56×10^{-4}	8
$Cr_2O_7^{2-}$	**JXUST-9**	H_2O	1.23×10^{-6}	This work
	$\{[Eu_3(L7)_3(HCOO)(OH)_2(DMF)]\cdot 3DMF\cdot 2H_2O\}_n$	H_2O	5.00×10^{-7}	6
	$[Eu(L1)(H_2O)]\cdot 1.5H_2O$	H_2O	1.25×10^{-6}	1
	$\{Eu(L3)(H_2O)(DMA)\}_n$	H_2O	6.05×10^{-5}	3
	$[Eu(L4)(DMF)(H_2O)(HCOO)]_n$	DMAc	6.06×10^{-6}	4
	$[Cd(L9)(L10)]\cdot H_2O$	H_2O	2.78×10^{-4}	8

H_3L1 = 3-(3,5-dicarboxylatobenzyloxy) benzoic acid;

H_3L2 = 3,5-(4-carboxybenzyloxy) benzoic acid;

H_5L3= 2,4-di(3′,5′-dicarboxylphenyl) benzoic acid;

H_2L4 = 4,4-(9,9-dimethyl-9H-fluorene-2,7-diyl) dibenzoic acid;

H_4L5 = 1,2,4,5-benzenetetracarboxylic acid;

L6 = 1,4-bis(1-(pyridin-4-ylmethyl)-1H-benzo[d]imidazol-2-yl) methyl benzene;

H_2L7 = 4,40-(4,40-bipyridine-2,6-diyl) dibenzoic acid;

H_2L8 = 2,5-bis-(1H-1,2,4-triazol-1-yl) terephthalic acid;

L9 = N,N′-bis(4-methyl-enepyridin-4-yl)-1,4-naphthalene dicarboxamide;

H_2L10 = 5-methylisophthalic acid;

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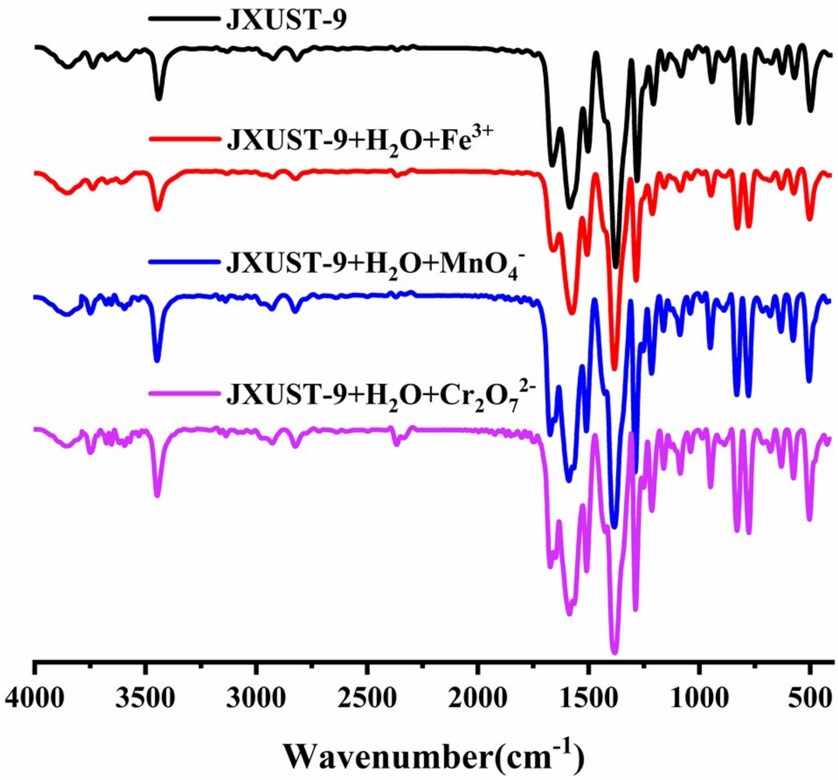


Fig. S1. IR spectra of **JXUST-9** and **JXUST-9** after soaked in different aqueous solutions containing Fe^{3+}, MnO_4^- and $Cr_2O_7^{2-}$ for 24 h, respectively.

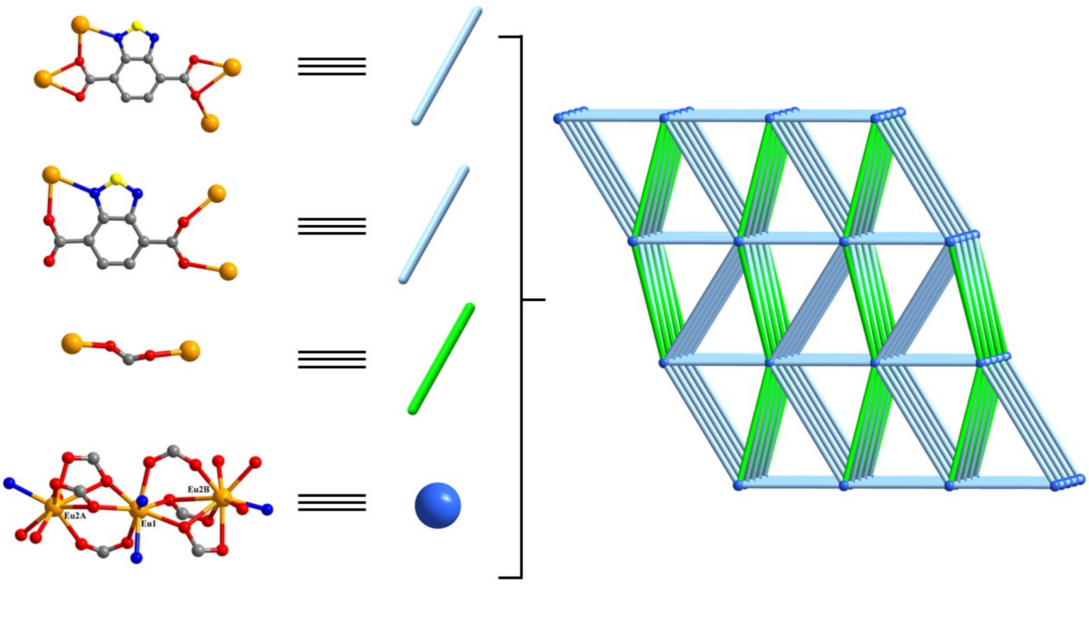


Fig. S2. The topological analysis and representations of **JXUST-9**.

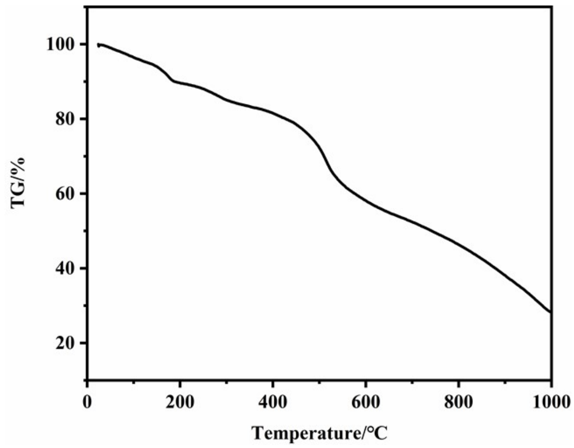
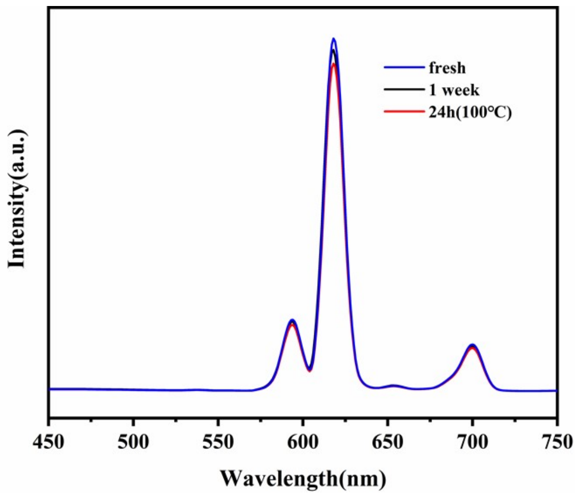
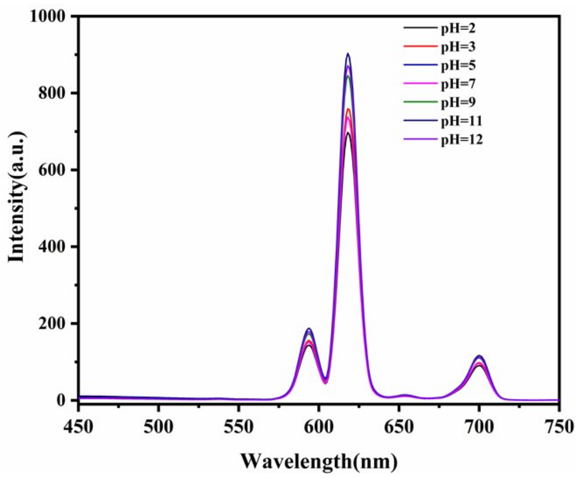


Fig. S3. The TGA curve of **JXUST-9**.

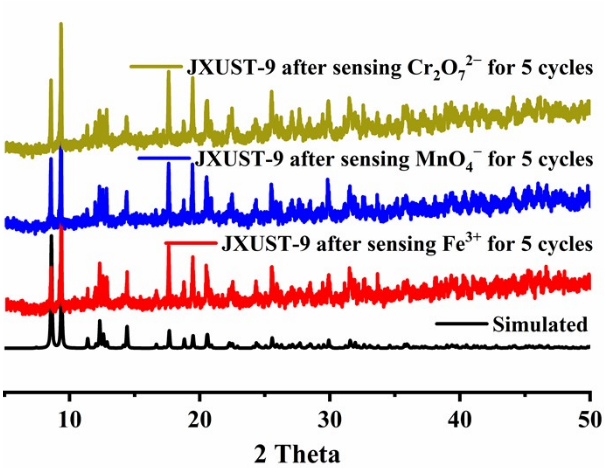


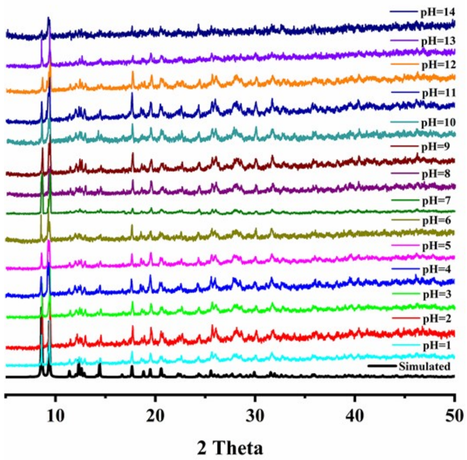
(a)



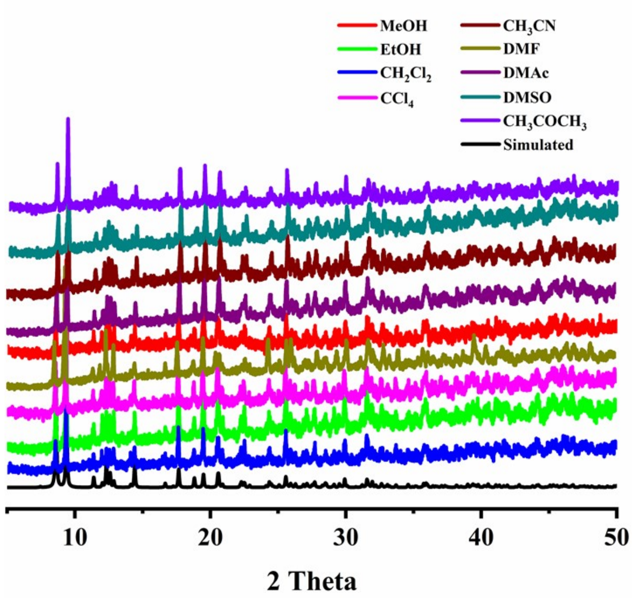
(b)

Fig. S4. (a) The emission spectra of **JXUST-9** soaked in water at room temperature for a week or soaked in boiling water for 24 h. (b) The emission spectra of **JXUST-9** in aqueous solution with different pH values.





(a) **(b)**



(c)

Fig. S5. (a) The PXRD patterns **JXUST-9** after sensing Fe^{3+}, MnO_4^- and $Cr_2O_7^{2-}$ for 5 cycles. (b) PXRD patterns of **JXUST-9** soaked in aqueous solutions with different pH values for 12 h. (c) PXRD patterns of **JXUST-9** soaked in common organic solvents for 24 h.

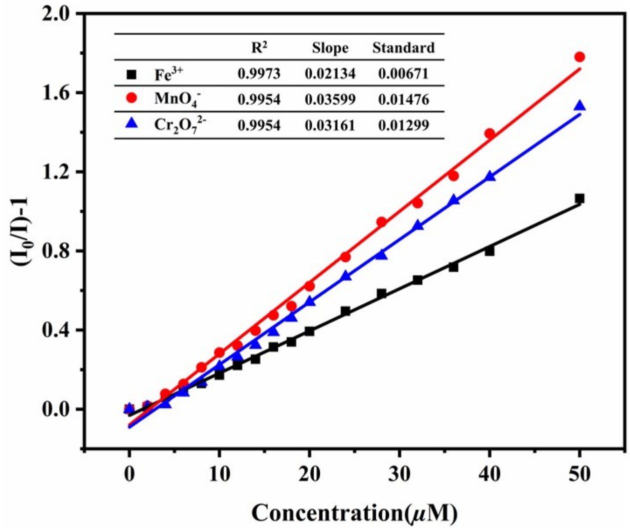
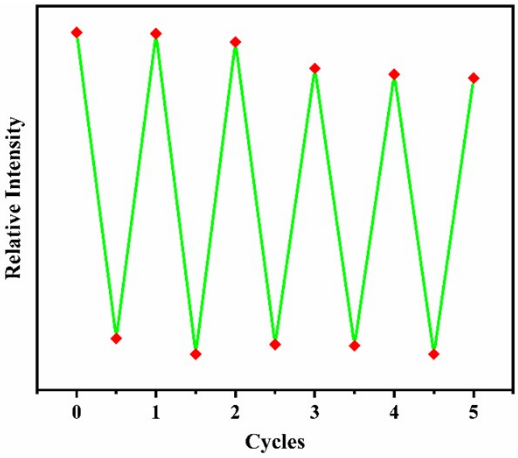
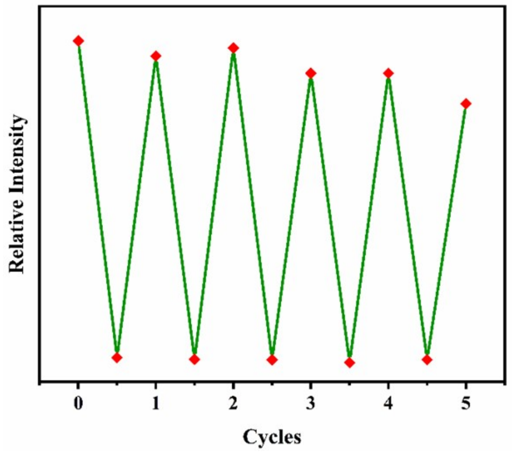


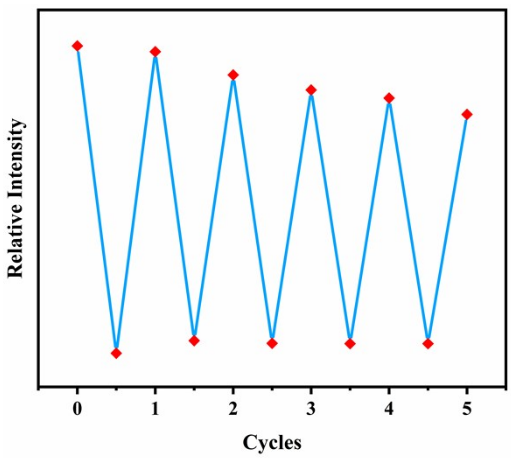
Fig. S6. Stern-Volmer plots of **JXUST-9** for Fe^{3+}, MnO_4^- and $Cr_2O_7^{2-}$.



(a)



(b)



(c)

Fig. S7. The relative fluorescence intensity of **JXUST-9** at 619 nm after five times of recycling toward Fe^{3+} (a), MnO_4^- (b) and $Cr_2O_7^{2-}$ (c) (λ_{ex} = 344 nm).

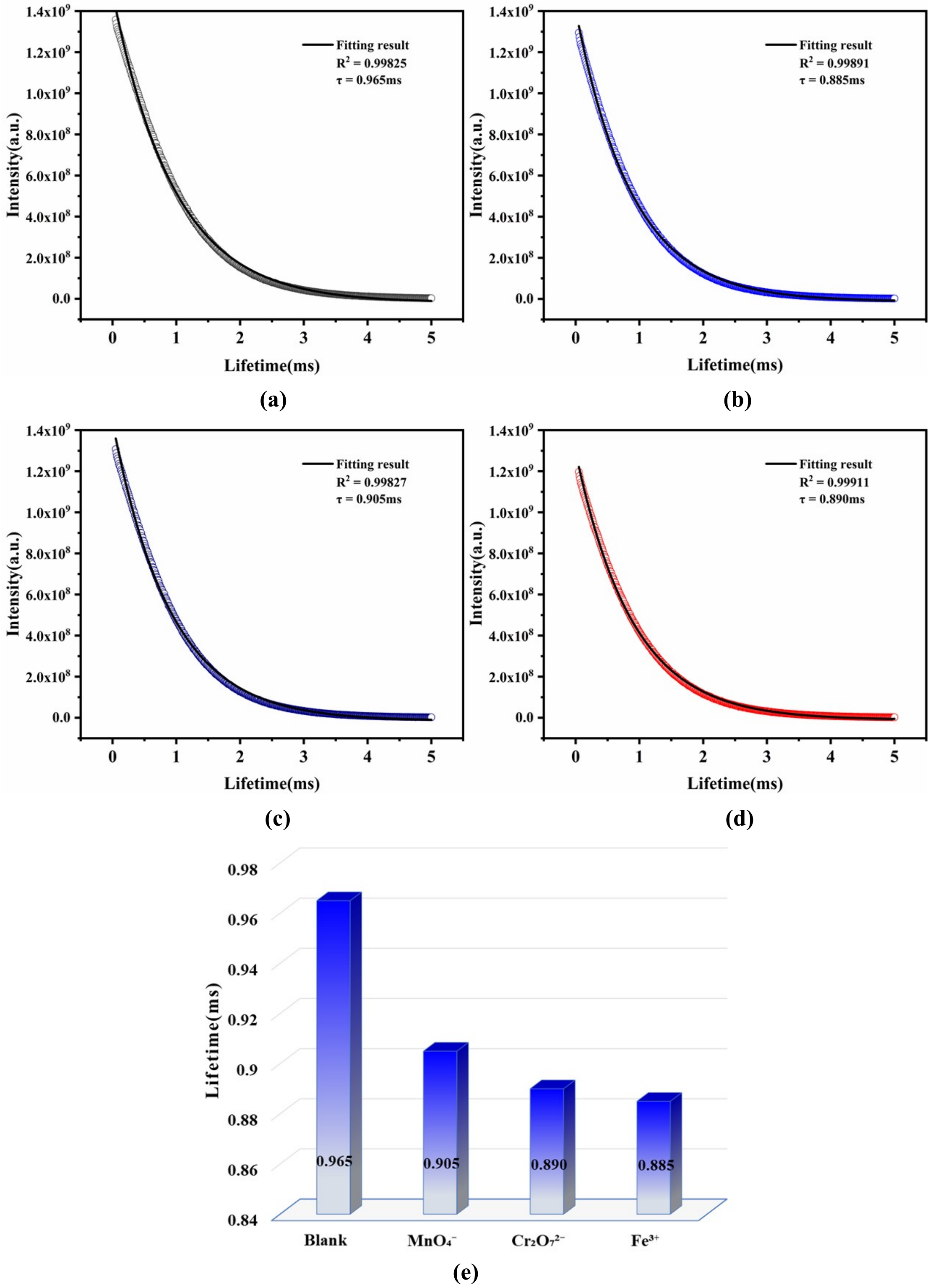


Fig. S8. The decay curves of **JXUST-9** (a), **JXUST-9**@Fe^{3+} (b), **JXUST-9**@MnO_4^- (c) and **JXUST-9**@$Cr_2O_7^{2-}$ (d) monitored at 619 nm, and the luminescence lifetime of **JXUST-9**, **JXUST-9**@Fe^{3+}, **JXUST-9**@MnO_4^- and **JXUST-9**@$Cr_2O_7^{2-}$ (e).

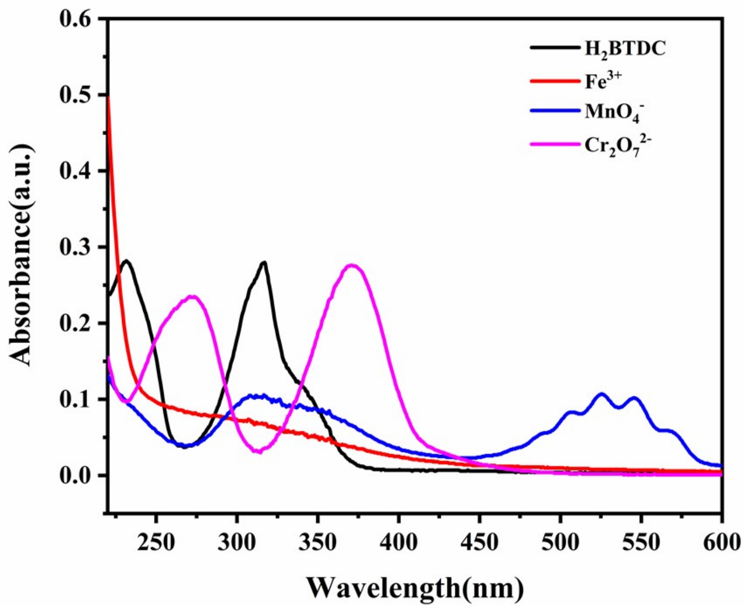


Fig. S9. The absorption spectra of H_2BTDC, Fe^{3+}, MnO_4^- and $Cr_2O_7^{2-}$ in aqueous solution.