Electronic Supplementary Information (ESI)

Chain-based fluorescent Tb^{III} metal-organic framework with good stability as a blue-shift and turn-on sensor toward $H_2PO_4^-$

Shixian Xu,[a]‡ Na Lu,[b]‡ Li Wang,[b] and Sui-Jun Liu*[b]

[a] College of Chemistry and Environmental Science, Shangrao Normal University, Shangrao 334001, Jiangxi Province, P. R. China

[b] School of Chemistry and Chemical Engineering, Jiangxi Provincial Key Laboratory of Functional Crystalline Materials Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, Jiangxi Province, P. R. China

---

**Corresponding author. E-mail: sjliu@jxust.edu.cn (S.-J. Liu). Tel: +86-797-8312204.*

‡These authors contributed equally to this work and should be considered co-first authors.

Table S1. Crystal data and structure refinements for **JXUST-52**.

Identification code	**JXUST-52**
Empirical formula	$C_{60}H_{32}N_6O_{16}S_3Tb_3$
Formula weight	1665.85
Temperature/K	293.15
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	8.7857(5)
b/Å	18.8668(11)
c/Å	20.7919(13)
α/°	113.758(2)
β/°	95.709(2)
γ/°	102.086(2)
Volume/Å^3	3018.7(3)
Z	2
D_{calc} g/cm^3	1.833
μ/mm^{-1}	3.654
Reflections collected/unique	44107/13756
R_{int}	0.0625
$R_1{}^a/wR_2{}^b[I>=2\sigma(I)]$	0.0562/0.1401
$R_1{}^a/wR_2{}^b$ [all data]	0.0786/0.1535
Goodness-of-fit on F^2	1.036

$^aR_1=\sum(||F_0|-|Fc||)/\sum|F_0|$; $^bwR_2=[\sum w(|F_0|^2-|Fc|^2)^2/(\sum w|F_0|^2)^2]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) for **JXUST-52**[a].

Tb1—O1^{i}	2.363(6)	O13^{v}—Tb2—O9^{vi}	75.92(17)
Tb1—O6^{iii}	2.410(6)	O13—Tb2—O9^{vi}	143.91(17)
Tb1—O7	2.397(6)	O13—Tb2—O13^{v}	68.06(19)
Tb1—O9^{iv}	2.515(6)	O13^{v}—Tb2—O14	81.37(16)
Tb1—O14^{ii}	2.413(5)	O13—Tb2—O14	103.33(16)
Tb1—O14	2.375(5)	O13—Tb2—O15	73.34(16)
Tb1—O15	2.369(5)	O13^{v}—Tb2—O15	123.32(16)
Tb1—O11^{v}	2.343(6)	O12—Tb2—O4	74.6(2)
O1^{i}—Tb1—O6^{iii}	153.9(2)	O12—Tb2—O5^{vii}	91.7(2)
O1^{i}—Tb1—O7	80.3(2)	O12—Tb2—O9^{vi}	86.2(2)
O1^{i}—Tb1—O9^{iv}	86.43(19)	O12—Tb2—O13	86.41(19)
O1^{i}—Tb1—O14	104.83(19)	O12—Tb2—O13^{v}	74.63(18)
O1^{i}—Tb1—O14^{ii}	73.81(19)	O12—Tb2—O14	148.52(19)
O1^{i}—Tb1—O15	69.70(18)	O12—Tb2—O15	142.06(19)
O6^{iii}—Tb1—O9^{iv}	71.49(19)	O14—Tb2—O4	136.85(18)
O6^{iii}—Tb1—O14^{ii}	84.84(19)	O14—Tb2—O9^{vi}	68.15(17)
O7—Tb1—O6^{iii}	108.0(2)	O14—Tb2—O15	68.89(16)
O7—Tb1—O9^{iv}	79.44(19)	O15—Tb2—O4	68.08(17)
O7—Tb1—O14^{ii}	138.88(17)	O15—Tb2—O9^{vi}	128.52(17)
O14—Tb1—O6^{iii}	79.66(18)	Tb3—O3	2.421(6)
O14—Tb1—O7	151.87(18)	Tb3—O4	2.551(6)
O14—Tb1—O9^{iv}	128.01(17)	Tb3—O8	2.300(6)
O14^{ii}—Tb1—O9^{iv}	67.72(16)	Tb3—O10^{ix}	2.318(5)
O14—Tb1—O14^{ii}	67.41(18)	Tb3—O13	2.345(5)
O15—Tb1—O6^{iii}	133.57(19)	Tb3—O15	2.369(5)
O15—Tb1—O7	88.58(18)	Tb3—O1W	2.408(7)
O15—Tb1—O9^{iv}	154.86(18)	O2^{viii}—Tb3—O3	91.5(2)
O15—Tb1—O14^{ii}	110.88(16)	O2^{viii}—Tb3—O4	75.1(2)
O15—Tb1—O14	62.28(17)	O2^{viii}—Tb3—O8	141.0(2)
O11^{v}—Tb1—O1^{i}	133.5(2)	O2^{viii}—Tb3—O10^{ix}	78.6(2)
O11^{v}—Tb1—O6^{iii}	72.1(2)	O2^{viii}—Tb3—O13	79.8(2)
O11^{v}—Tb1—O7	73.5(2)	O2^{viii}—Tb3—O15	139.6(2)
O11^{v}—Tb1—O9^{iv}	124.3(2)	O2^{viii}—Tb3—O1W	71.7(3)
O11^{v}—Tb1—O14	83.85(19)	O3—Tb3—O4	52.36(19)
O11^{v}—Tb1—O14^{ii}	146.07(19)	O8—Tb3—O3	93.5(2)
O11^{v}—Tb1—O15	71.8(2)	O8—Tb3—O4	135.5(2)
Tb2—O4	2.472(5)	O8—Tb3—O10^{ix}	85.6(2)
Tb2—O5^{vi}	2.305(6)	O8—Tb3—O13	130.4(2)
Tb2—O9^{vii}	2.555(5)	O8—Tb3—O15	78.7(2)

Tb2—O13^{v}	2.333(5)	O8—Tb3—O1W	71.6(2)
Tb2—O13	2.313(5)	O10^{ix}—Tb3—O3	162.5(2)
Tb2—O12	2.260(5)	O10^{ix}—Tb3—O4	135.86(18)
Tb2—O14	2.337(5)	O10^{ix}—Tb3—O13	75.72(18)
Tb2—O15	2.370(5)	O10^{ix}—Tb3—O15	120.8(18)
O4—Tb2—O9^{vi}	143.19(18)	O10^{ix}—Tb3—O1W	84.9(2)
O5^{vii}—Tb2—O4	75.1(2)	O13—Tb3—O3	116.96(19)
O5^{vii}—Tb2—O9^{vi}	74.4(2)	O13—Tb3—O4	65.20(17)
O5^{vii}—Tb2—O13	141.10(19)	O13—Tb3—O15	72.78(17)
O5^{vii}—Tb2—O13^{v}	148.00(19)	O13—Tb3—O1W	148.2(2)
O5^{vii}—Tb2—O14	98.4(2)	O15—Tb3—O3	75.9(2)
O5^{vii}—Tb2—O15	85.2(2)	O15—Tb3—O1W	139.0(2)
O13—Tb2—O4	66.97(17)	O1W—Tb3—O3	78.3(3)
O13^{v}—Tb2—O4	126.18(17)	O1W—Tb3—O4	118.5(2)

[a]Symmetry codes: (i) 1-*x*, -*y*, 1-*z*; (ii) 1-*x*, -*y*, -*z*; (iii) 2-*x*, 1-*y*, 1-*z*; (iv) +*x*, 1+*y*, 1+*z*; (v) 2-*x*, -*y*, -*z*; (vi) -1+*x*, -1+*y*, -1+*z*; (vii) 1-*x*, -1-*y*, -1-*z*; (viii) 2-*x*, -*y*, -1-*z*; (ix) 1+*x*, 1+*y*, 1+*z*.

Table S3. The coordination configuration of Tb^{III} ions in **JXUST-52**.

Ions	Label	Shape	Symmetry	Distortion (τ)
	OP-8	Octagon	D_{8h}	30.754
	HPY-8	Heptagonal pyramid	C_{7v}	23.092
	HBPY-8	Hexagonal bipyramid	D_{6h}	15.865
	CU-8	Cube	O_h	10.983
	SAPR-8	Square antiprism	D_{4d}	3.878
	TDD-8	**Triangular dodecahedron**	$\boldsymbol{D_{2d}}$	**1.218**
Tb1	JGBF-8	Johnson gyrobifastigium J26	D_{2d}	11.966
	JETBPY-8	Johnson elongated triangular bipyramid J14	D_{3h}	26.460
	JBTPR-8	Biaugmented trigonal prism J50	C_{2v}	2.520
	BTPR-8	Biaugmented trigonal prism	C_{2v}	2.565
	JSD-8	Snub diphenoid J84	D_{2d}	2.830
	TT-8	Triakis tetrahedron	T_d	11.405
	ETBPY-8	Elongated trigonal bipyramid	D_{3h}	24.329
	OP-8	Octagon	D_{8h}	32.138
	HPY-8	Heptagonal pyramid	C_{7v}	23.410
	HBPY-8	Hexagonal bipyramid	D_{6h}	12.456
	CU-8	Cube	O_h	6.524
	SAPR-8	**Square antiprism**	$\boldsymbol{D_{4d}}$	**1.499**
	TDD-8	Triangular dodecahedron	D_{2d}	1.890
Tb2	JGBF-8	Johnson gyrobifastigium J26	D_{2d}	14.119
	JETBPY-8	Johnson elongated triangular bipyramid J14	D_{3h}	27.074
	JBTPR-8	Biaugmented trigonal prism J50	C_{2v}	3.305
	BTPR-8	Biaugmented trigonal prism	C_{2v}	2.753
	JSD-8	Snub diphenoid J84	D_{2d}	5.405
	TT-8	Triakis tetrahedron	T_d	7.122
	ETBPY-8	Elongated trigonal bipyramid	D_{3h}	23.765
	OP-8	Octagon	D_{8h}	29.753
	HPY-8	Heptagonal pyramid	C_{7v}	22.116
	HBPY-8	Hexagonal bipyramid	D_{6h}	13.858
	CU-8	Cube	O_h	8.921
	SAPR-8	Square antiprism	D_{4d}	2.233
	TDD-8	Triangular dodecahedron	D_{2d}	2.811
Tb3	JGBF-8	Johnson gyrobifastigium J26	D_{2d}	12.051
	JETBPY-8	Johnson elongated triangular bipyramid J14	D_{3h}	26.651
	JBTPR-8	Biaugmented trigonal prism J50	C_{2v}	2.068
	BTPR-8	**Biaugmented trigonal prism**	$\boldsymbol{C_{2v}}$	**1.582**
	JSD-8	Snub diphenoid J84	D_{2d}	4.542
	TT-8	Triakis tetrahedron	T_d	9.599
	ETBPY-8	Elongated trigonal bipyramid	D_{3h}	21.862

Table S4. The sensing properties of LMOF with other reported sensors for anions.

LMOF	Fluorescent Response	Anions	Detection Limit	Reference
JXUST-52	Turn-on response	$H_2PO_4^-$	0.016 mM	This work
Eu-MOF	Turn-off response	$H_2PO_4^-$	0.70 mM	S1
JXUST-13	Turn-on response	$H_2PO_4^-$	2.70 μmol/L	S2
UiO-66-NH_2	Turn-on response	PO_4^{3-}	1.25 mM	S3
Cd-MOF	Turn-off response	ClO^-	0.18 μM	S4
Eu-MOF	Turn-off response	$Cr_2O_7^{2-}$	1.14×10^{-4} mol L^{-1}	S5
Zn-MOF	Turn-off response	CrO_4^{2-}	5.25 μM	S6
CP-1	Turn-off response	MnO_4^-	1.291 μM	S7
Al-MOF	Turn-on response	F^-	0.31 μM	S8

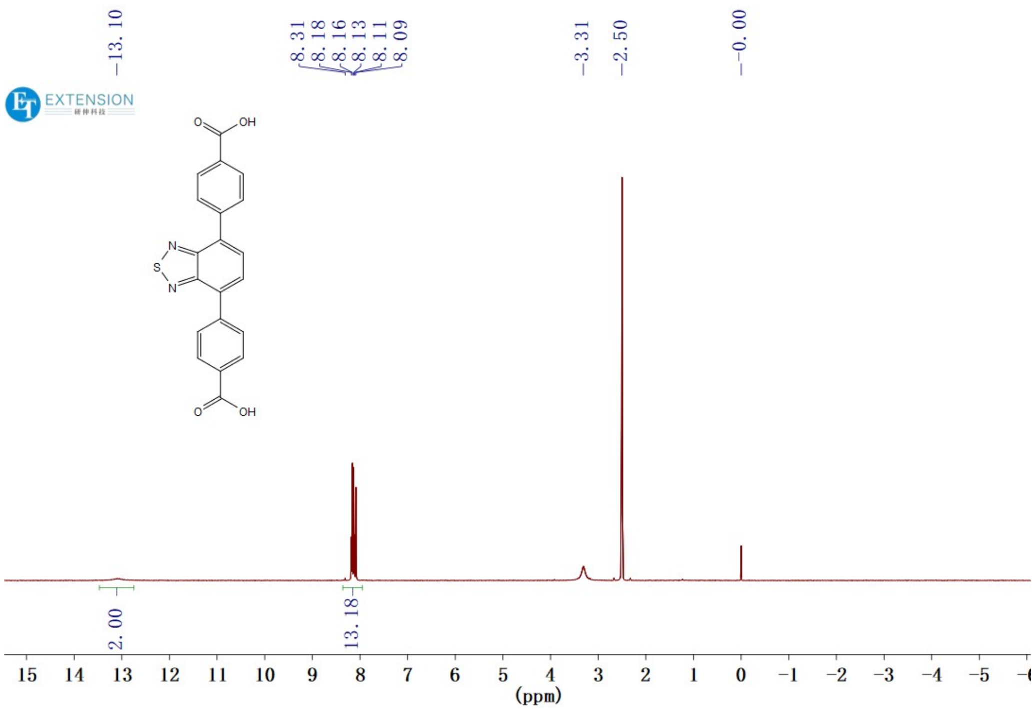


Fig. S1 ^{1}H NMR spectrum of H_2BTDB.

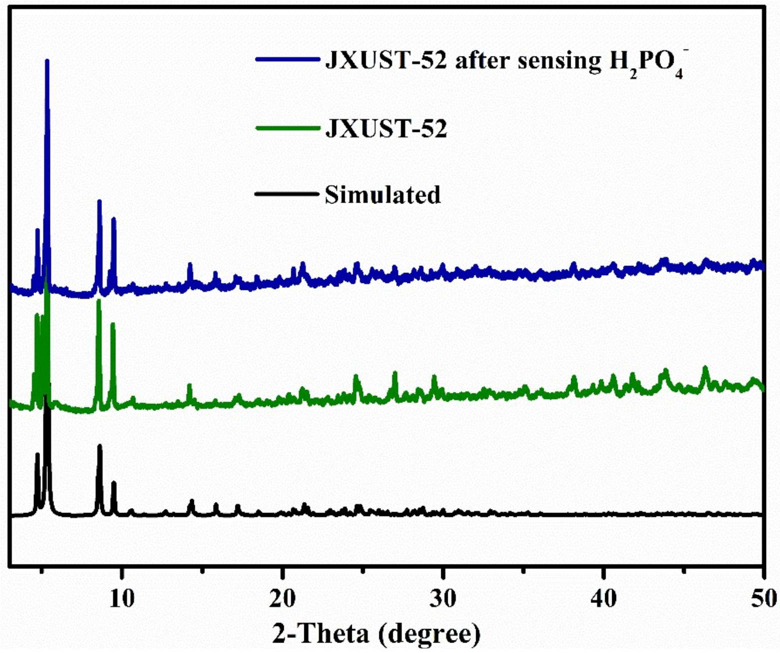


Fig. S2 The PXRD patterns of **JXUST-52** and **JXUST-52**@$H_2PO_4^-$.

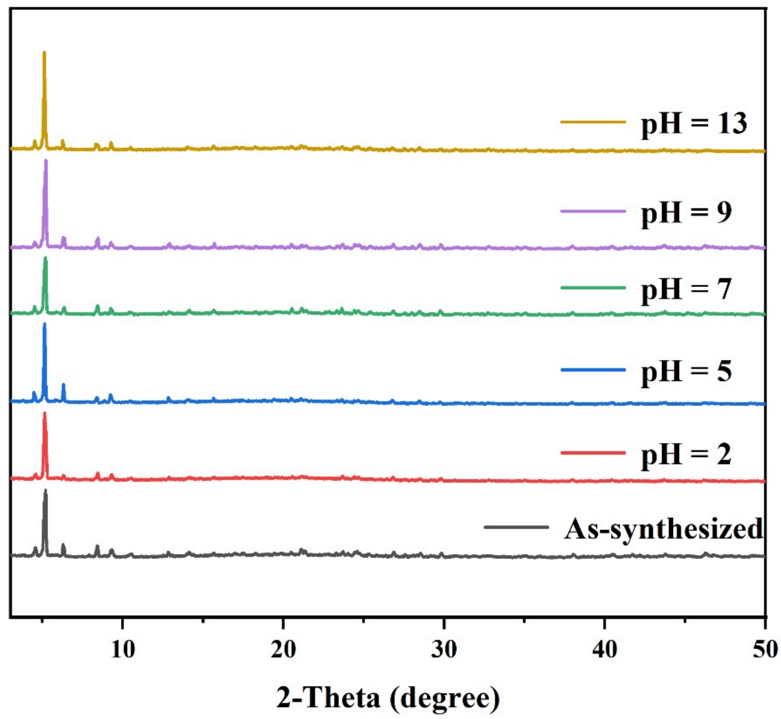


Fig. S3 The experimental PXRD patterns of **JXUST-52** immersed in aqueous solutions with different pH values for 24 hours.

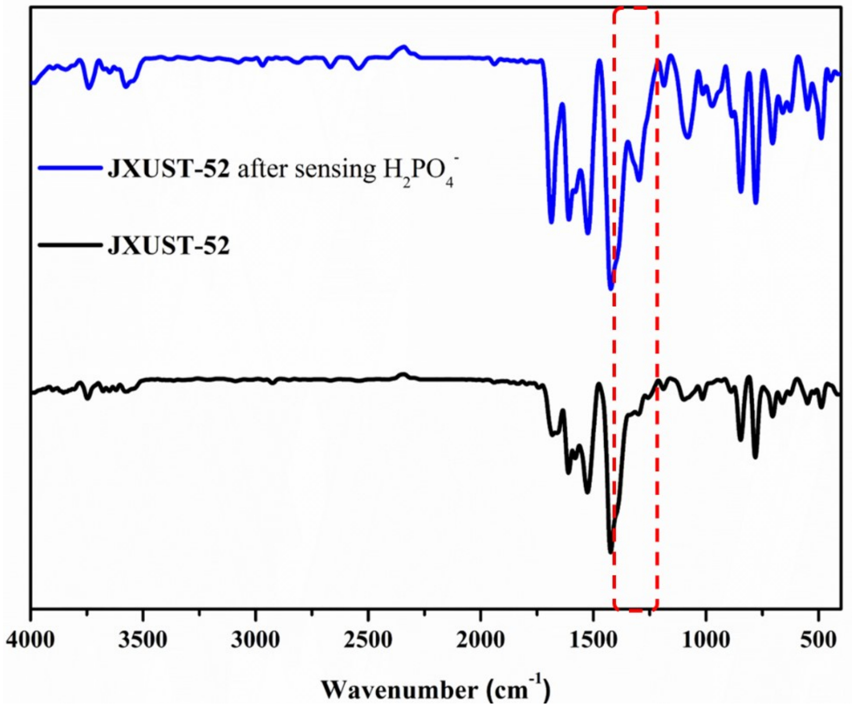


Fig. S4 IR spectra of **JXUST-52** and **JXUST-52**@$H_2PO_4^-$.

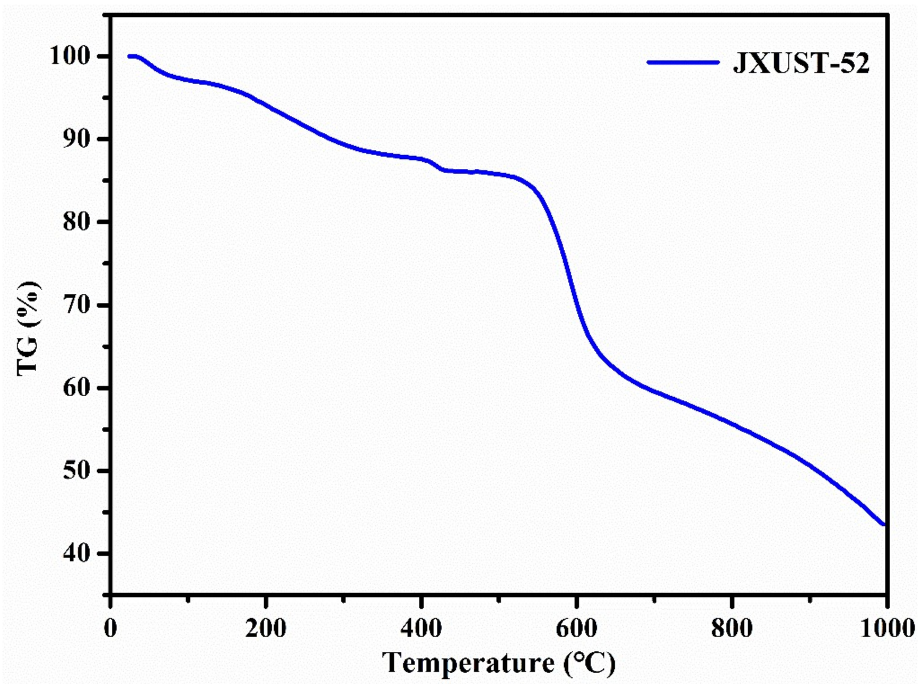


Fig. S5 The TGA curve of **JXUST-52**.

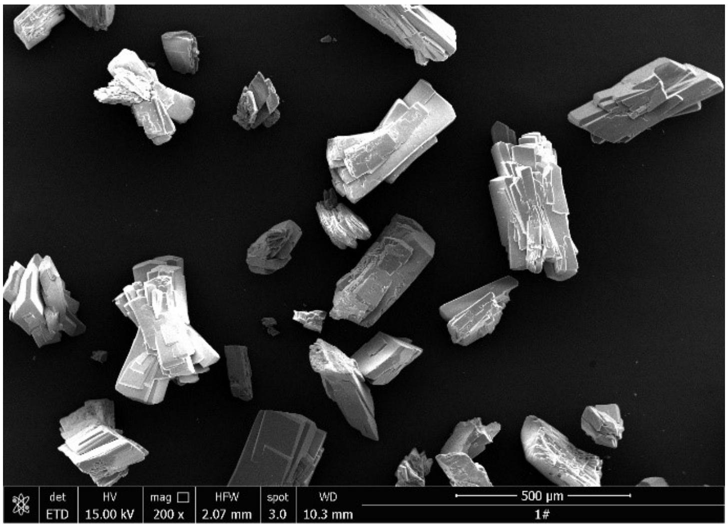


Fig. S6 The SEM image of the crystalline sample for **JXUST-52**.

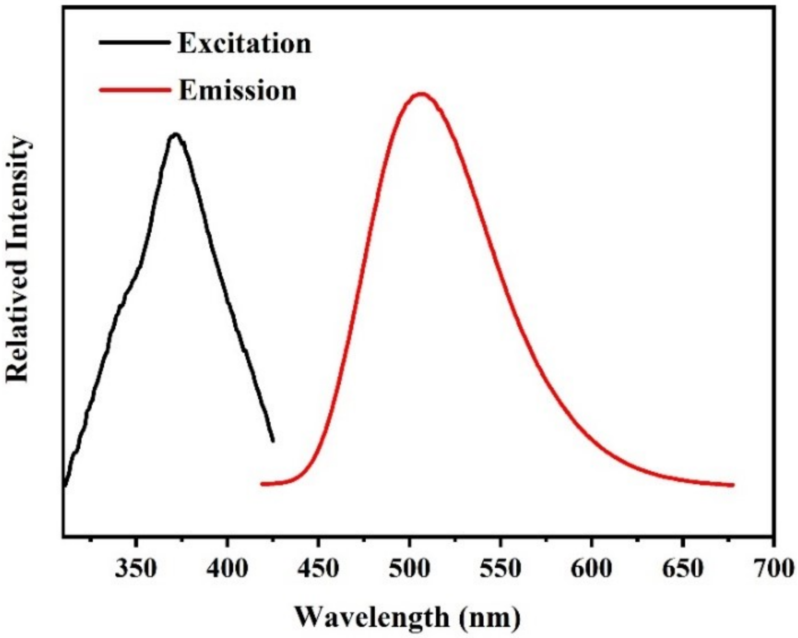


Fig. S7 The excitation and emission spectra of H_2BTDB.

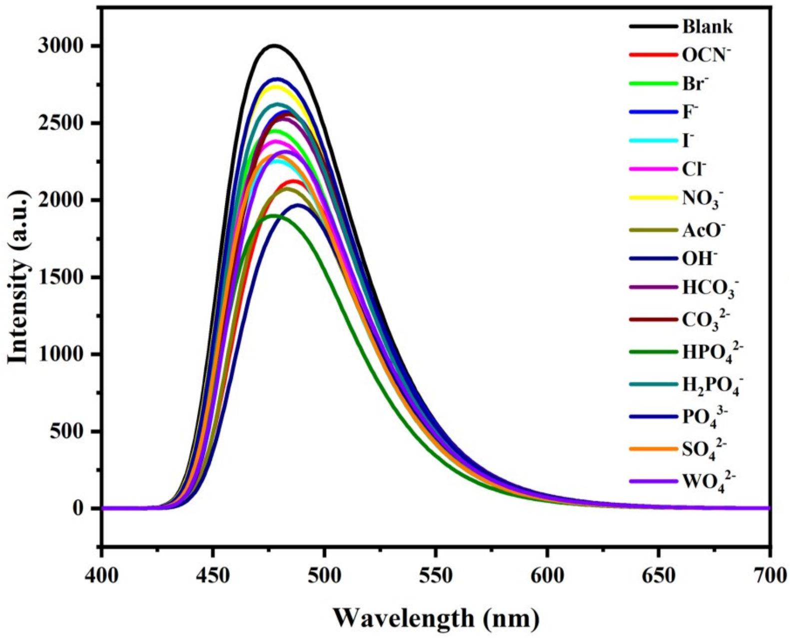


Fig. S8 The fluorescence intensities of H_2BTDB upon addition of different anions in DMF solutions.

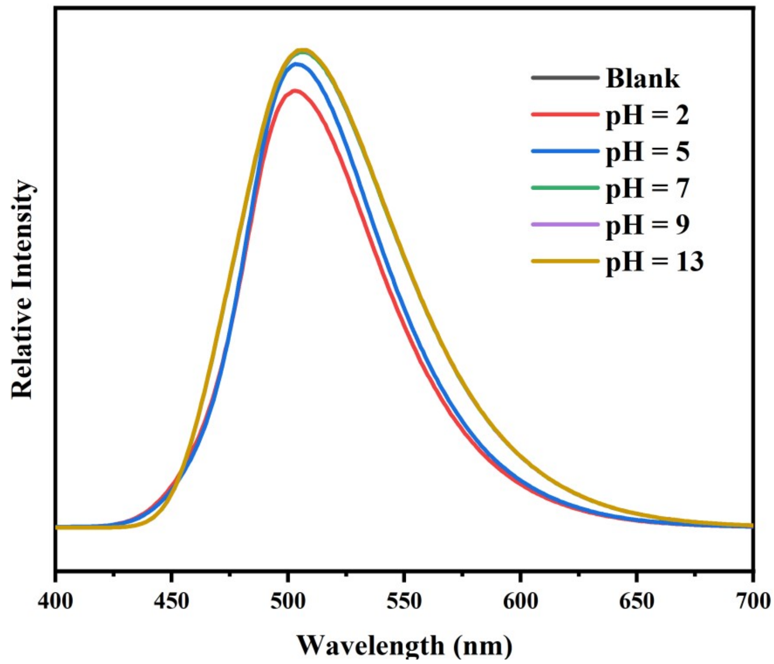
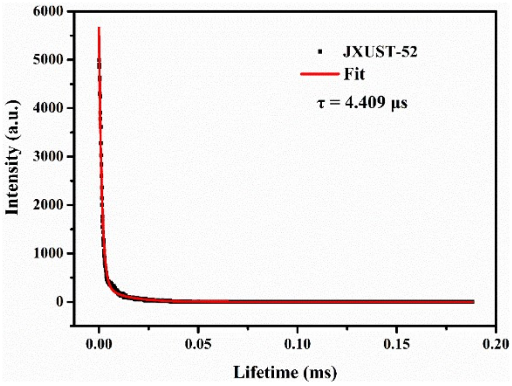
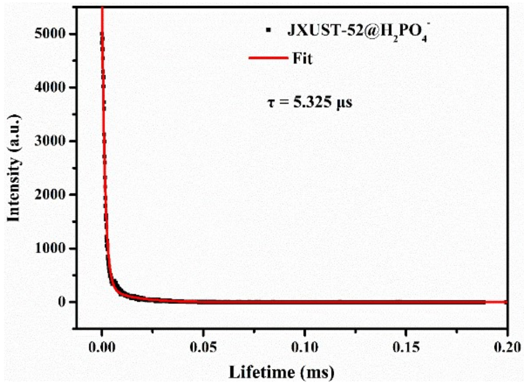


Fig. S9 The fluorescence intensities of **JXUST-52** immersed in aqueous solution with different pH values.



(a)



(b)

Fig. S10 The fluorescence lifetime decay diagrams of (a) **JXUST-52** and (b) **JXUST-52**@ $H_2PO_4^-$.

References

S1 T. Wiwasuku, A. Chuaephon, T. Puangmali, J. Boonmak, S. Ittisanronnachai, V. Promarak and S. Youngme, *RSC Adv*., 2023, **13**, 10384-10396.

S2 S. Yao, H. Xu, T. Zheng, Y. Li, H. Huang, J. Wang, J. Chen, S. Liu, and H. Wen, *Chin. Chem. Lett*., 2023, **34**, 107532.

S3 J. Yang, Y. Dai, X. Zhu, Z. Wang, Y. Li, Q. Zhuang, J. Shi and J. Gu, *J. Mater. Chem. A*., 2015, **3**, 7445-7452.

S4 Y. N. Wang, H. Xu, S. D. Wang, R. Y. Mao, L. M. Wen, S. Y. Wang, L. J. Liu, Y. Sun, S. Q. Lu, F. Wang and Q. F. Yang, *Spectrochim. Acta A Mol. Biomol. Spectrosc*., 2023, **286**, 121952.

S5 J. Y. Zou, L. Li, S. Y. You, Y. W. Liu, H. M. Cui, J. Z. Cui and S. W. Zhang, *Dalton Trans*., 2018, **47**, 15694-15702.

S6 S. Chen, Y. Dong, H. Song and L. Gui, *J. Solid State Chem*., 2023, **328**, 124335.

S7 F. Su, X. Y. Liu, S. D. Li, L. Sun, L. T. Wu, C. Han and Z. J. Wang, *J. Mol. Struct*., 2024, **1298**, 136975.

S8 D. H. Xie, X. Ge, W. X. Qin and Y. X. Zhang, *Chinese J. Chem. Phys*., 2021, **34**, 227-237.