

Efficient detection of Al^{3+} and $\text{B}_4\text{O}_7^{2-}$ over trigonal prism In(III) complex

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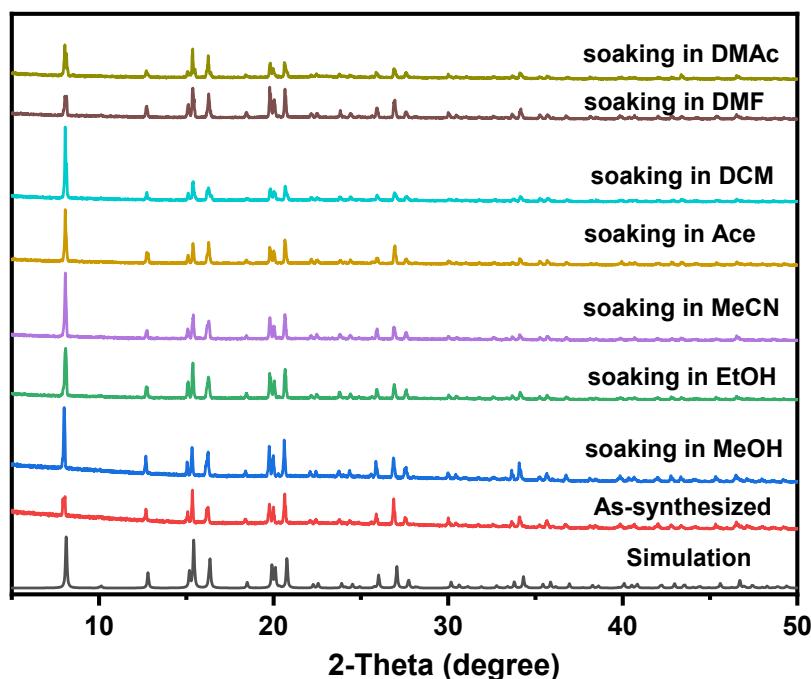


Fig. S1 The Powder X-ray diffraction patterns of **1** immersing in common solvents: methanol (MeOH), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), ethanol (EtOH), acetonitrile (MeCN), dichloromethane (DCM) and acetone (Ace) for 24 h.

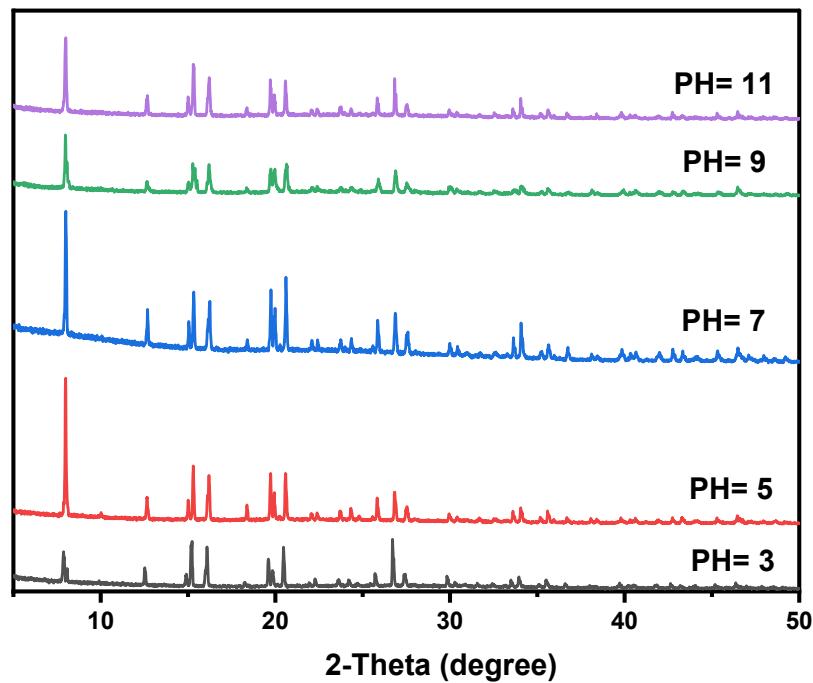


Fig. S2 The Powder X-ray diffraction patterns of **1** immersing in MeOH in different PH values.

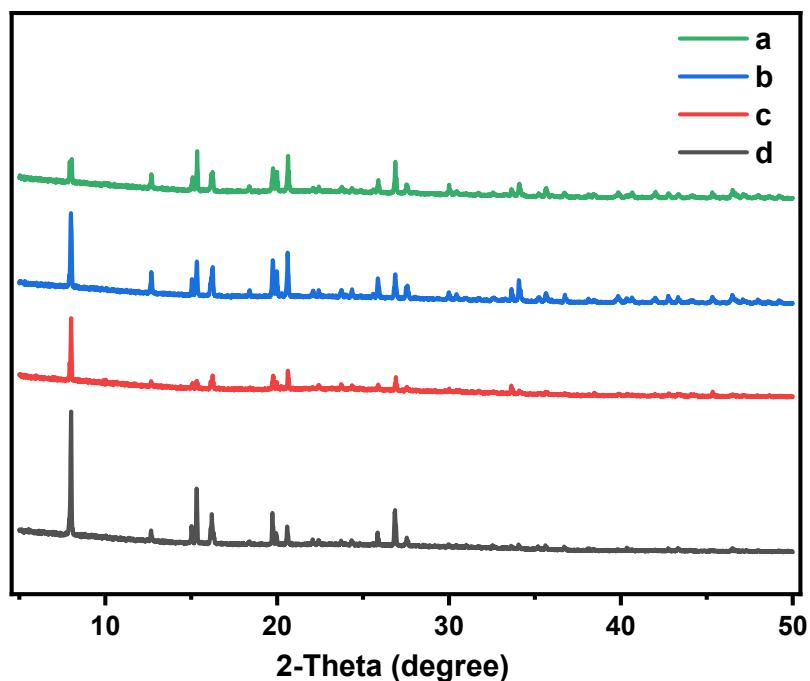


Fig. S3 The PXRD patterns of (a) as-synthesized. (b) **1** after soaked in MeOH for 48 h. (c) **1** after ultrasonic sound in MeOH containing Al^{3+} (10^{-3} M) for 25 min. (d) **1** after ultrasonic sound in MeOH containing $\text{B}_4\text{O}_7^{2-}$ (10^{-3} M) for 25 min.

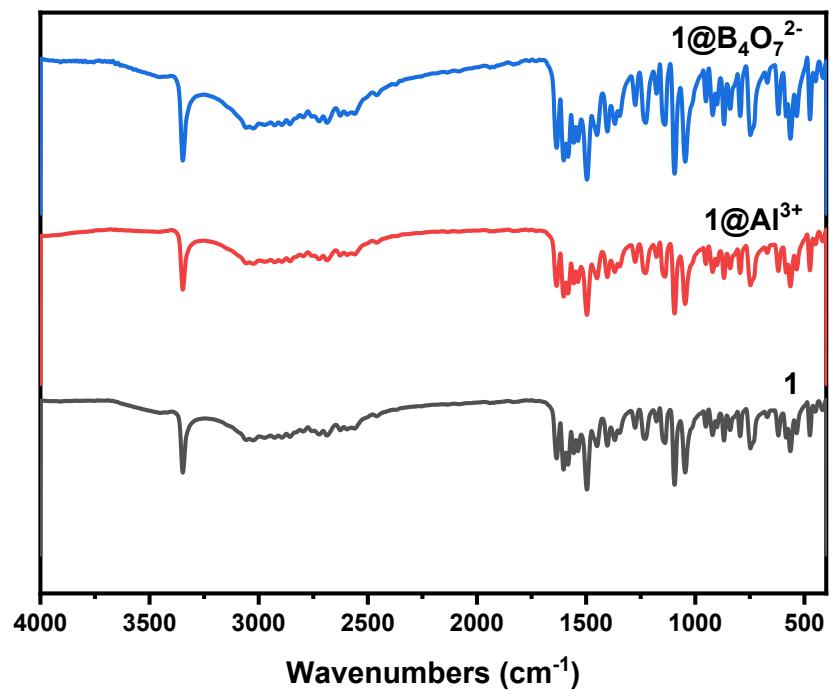


Fig. S4 The FT-IR spectra of **1** before and after being ultrasonic in MeOH containing Al^{3+} and $\text{B}_4\text{O}_7^{2-}$.

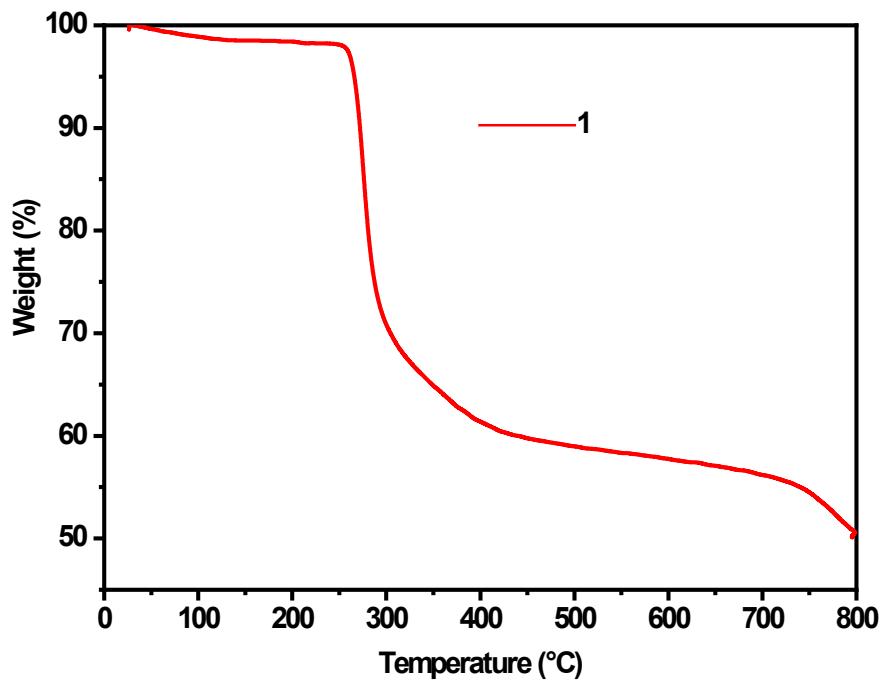


Fig. S5 TGA plot of **1** under N_2 condition.

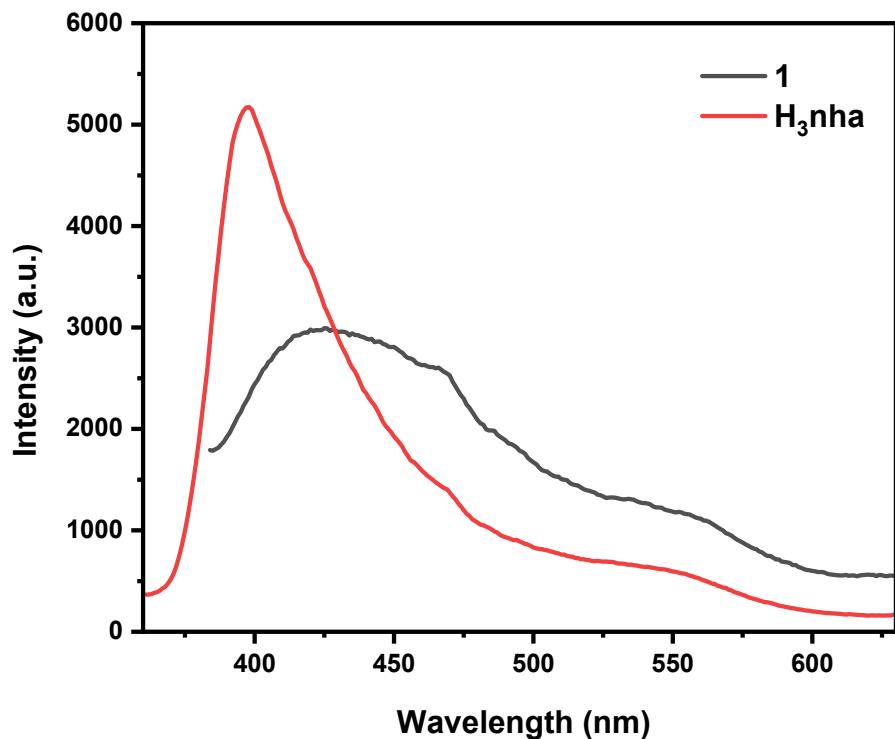


Fig. S6 Solid state luminescence spectra of H_3nha ($\lambda_{\text{ex}}=325 \text{ nm}$) and **1** ($\lambda_{\text{ex}}=330 \text{ nm}$)

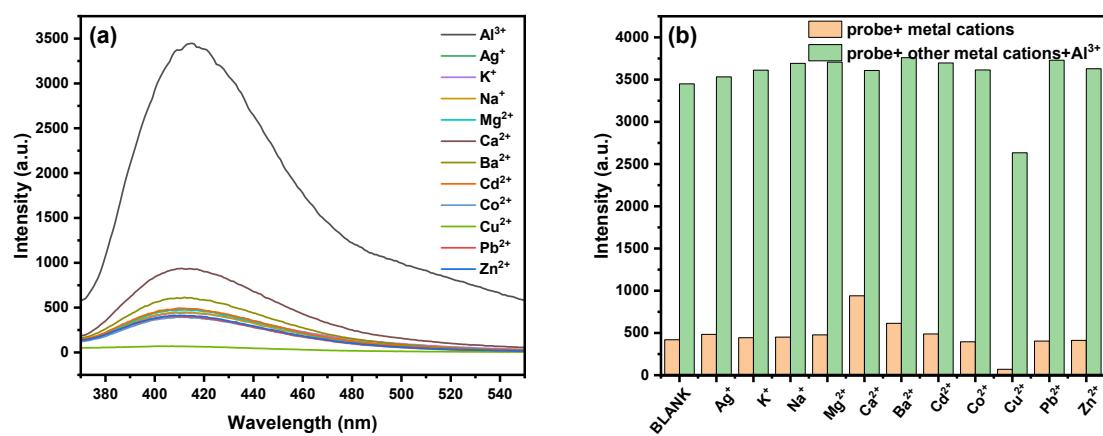


Fig. S7 (a) Luminescence spectra of H_3nha (10^{-4} M) in MeOH upon the addition of different metal ions; (b) Luminescence intensities at 325 nm of H_3nha (10^{-4} M) in MeOH in the presence of only Al^{3+} (10^{-3} M) and Al^{3+} with the other metal ions (10^{-3} M).

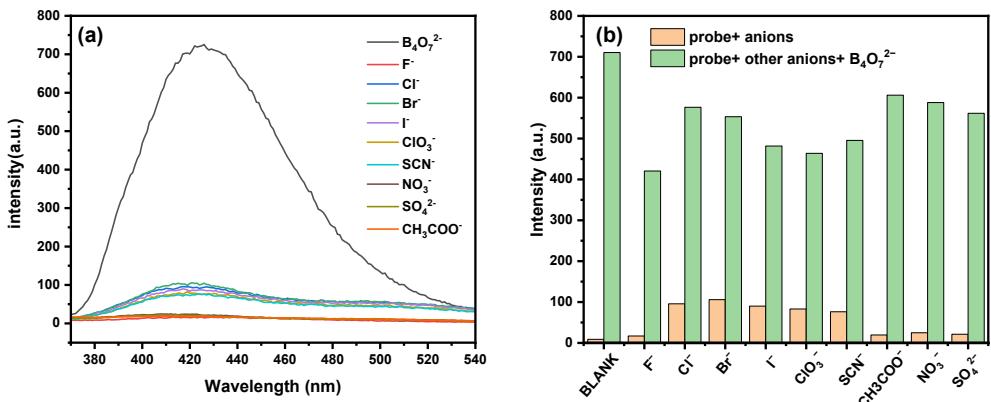


Fig. S8 (a) Luminescence spectra of H_3nha (10^{-4} M) in solution (MeOH:H₂O, v/v = 9:1) upon the addition of different non-metal anions; (b) Luminescence intensities at 325 nm of H_3nha (10^{-4} M) in solution (MeOH:H₂O, v/v = 9:1) in the presence of only $\text{B}_4\text{O}_7^{2-}$ (10^{-3} M) and $\text{B}_4\text{O}_7^{2-}$ with the other anions (10^{-3} M).

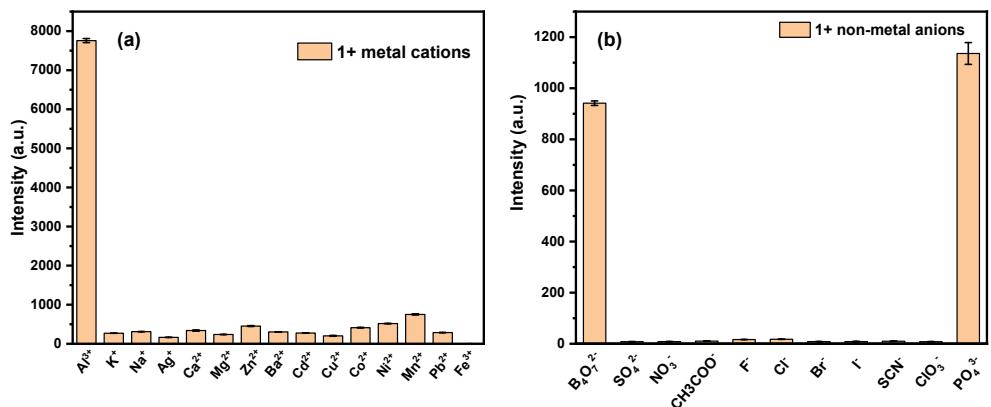


Fig. S9 Luminescence spectra of **1** in MeOH upon the addition of (a) different metal ions and (b) different non-metal anions;

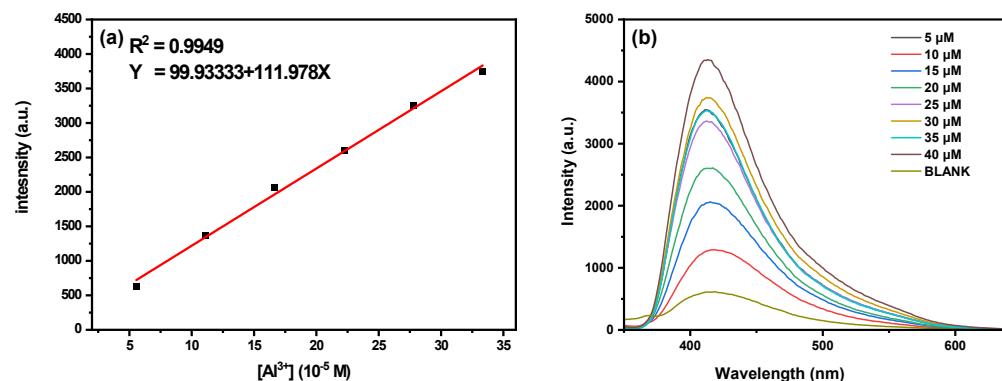


Fig. S10 (a) Linear relationship of the luminescence intensity at 330 nm of **1** with the concentration of Al^{3+} . (b) The luminescence spectra of **1** in MeOH with different concentration of Al^{3+} .

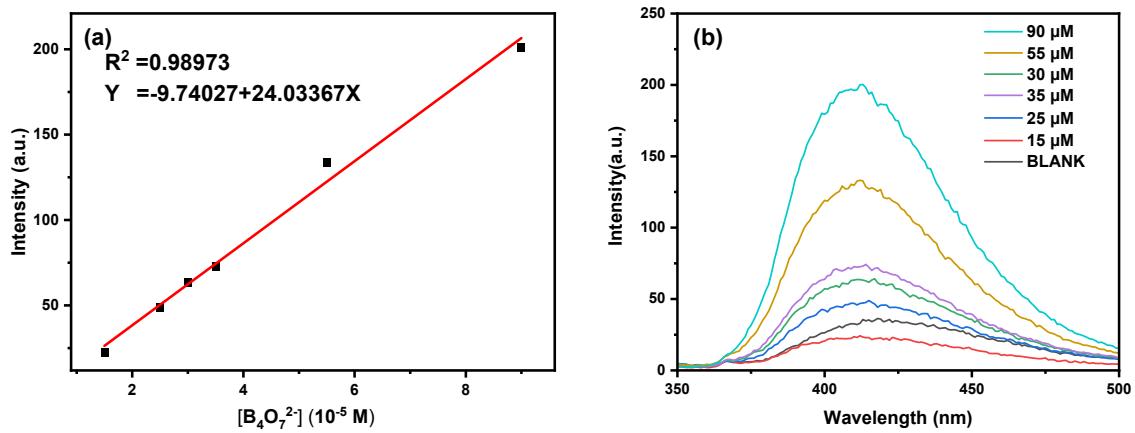


Fig.S11 (a) The luminescence spectra of **1** in solution (MeOH:H₂O, v/v = 9:1) with different concentration of B₄O₇²⁻ (b) Linear relationship of the luminescence intensity at 330 nm of **1** with the concentration of B₄O₇²⁻.

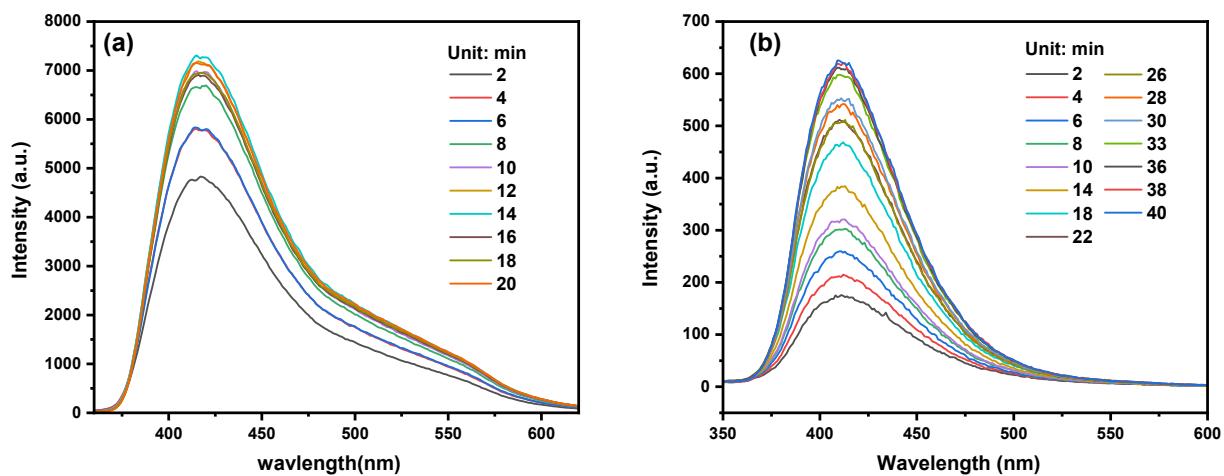


Fig.S12 The luminescence intensity of (a) **1**@Al³⁺ and (b) **1**@B₄O₇²⁻ with the increase of time.

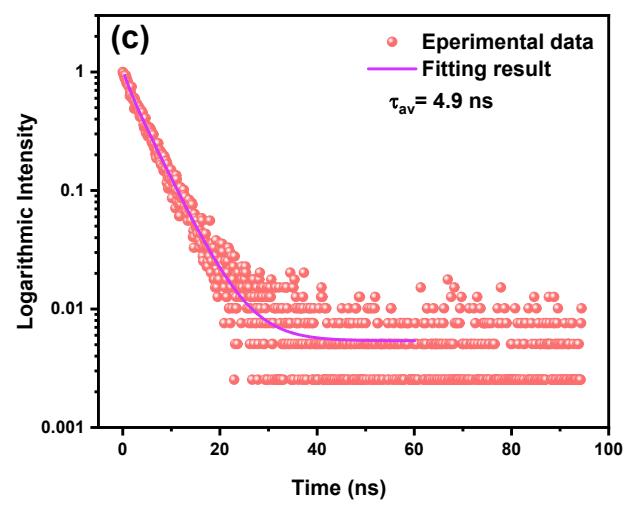
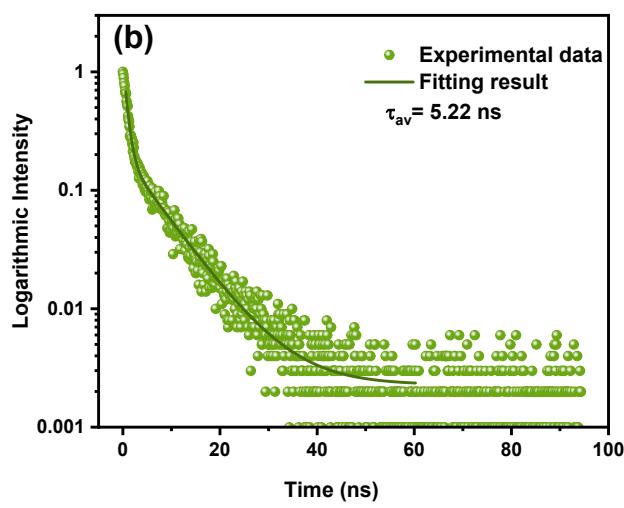
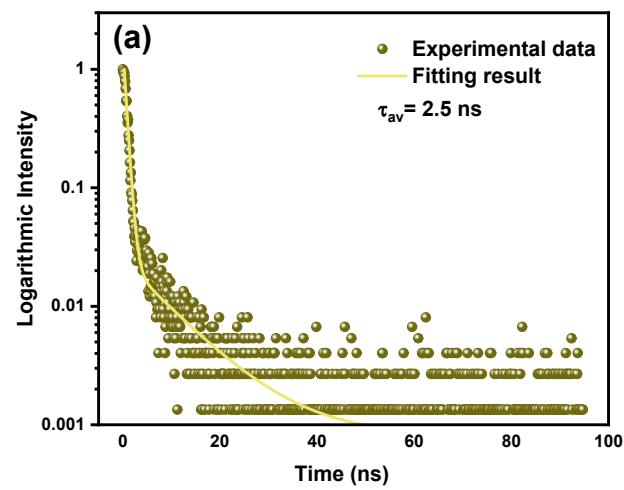


Fig. S13 The time resolved luminescence decay corresponding fitted lines of **1** (a) in MeOH, (b) **1@Al³⁺**, (c) **1@B₄O₇²⁻**.

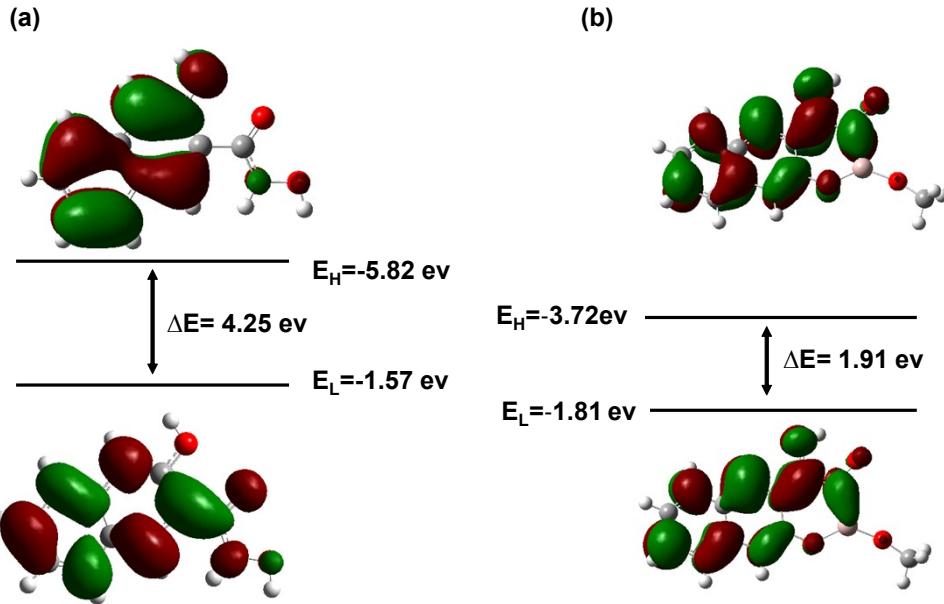


Fig. S14 HOMO and LUMO energies for **1** and **1@Al³⁺**.

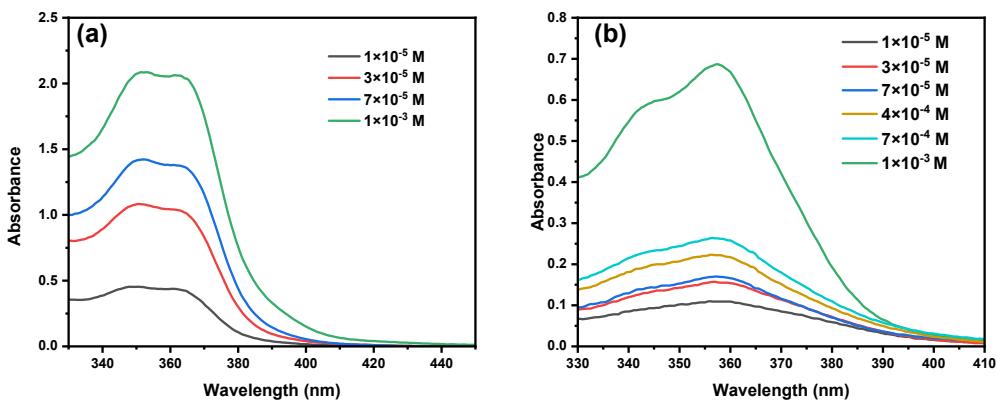


Fig. S15 The absorption spectra of **1** by addition of different concentrations of (a) Al³⁺ and (b) B₄O₇²⁻.

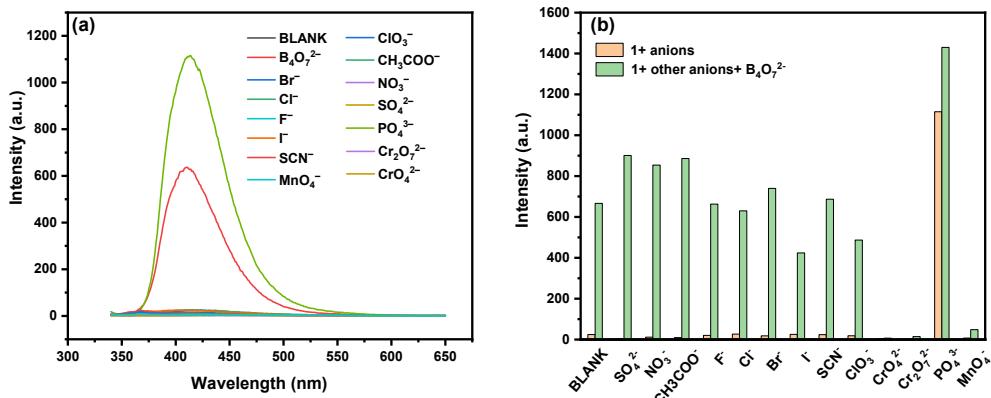


Fig. S16 (a) Luminescence spectra of **1** in solvent (MeOH:H₂O, v/v = 9:1) upon the addition of different non-metal anions; (b) Luminescence intensities at 330 nm of **1** in the presence of only B₄O₇²⁻ (10⁻³ M) and B₄O₇²⁻ with the other non-metal anions (10⁻³ M).

Table S1 The continuous shape measures value calculated using SHAPE 2.1.

| Complex | HP(D_{6h}) | PPY(C_{5v}) | OC(O_h) | TPR(D_{3h}) | JPPY (C_{5v}) |
|----------|--------------------------------|---------------------------------|-----------------------------|---------------------------------|-----------------------------------|
| 1 | 35.956 | 19.726 | 5.131 | 4.439 | 23.839 |

Table S2 Selected bond lengths (Å) for **1**.

| Selected bond lengths | |
|-----------------------|------------|
| In(1)–O(1) | 2.1540(19) |
| In(1)–O(2) | 2.132(2) |
| N(1)–O(1) | 1.372(3) |
| C(1)–O(2) | 1.268(3) |
| C(1)–N(1) | 1.315(3) |

Table S3 Comparison of various sensors for the detection of Al^{3+} and $\text{B}_4\text{O}_7^{2-}$.

| | Complex | Sensing type | Identification substance | LOD | Reference |
|---|---|--------------|-----------------------------|---------------------|-----------|
| 1 | A-curcumin@MOF-5 | Turn-on | Al^{3+} | 3.10 μM | 1 |
| 2 | B-curcumin@MOF-5 | Turn-on | Al^{3+} | 2.84 μM | 1 |
| 3 | Eu^{3+} @UiO-66-(COOH) ₂ /OH | Turn-off | Al^{3+} | 0.36 μM | 2 |
| 4 | $[\text{Zn}(\text{ICA})_2(\text{DMF})(\text{H}_2\text{O})_3]$ | Turn-on | Al^{3+} | 0.607 μM | 3 |
| 5 | {[Cd(2-amino-1,4-benzenedicarboxylate)(4,4'azopyridine)] (DMA)} _n | Turn-on | Al^{3+} | 0.38 μM | 4 |
| 6 | {[$\text{Zn}_2(\text{NDC})_2(4\text{bppyytz})$]1.5DMF} | Turn-on | Al^{3+} | 2.9 μM | 5 |
| 7 | $\text{In}(\text{H}_2\text{nha})_3$ | Turn-on | Al^{3+} | 1.3 μM | This work |
| 8 | {[$\text{Tb}(\text{dppa})(\text{H}_2\text{O})_2$] dima $\text{H}_2\text{O}\cdot 0.5\text{O}$ } _n | Turn-on | $\text{B}_4\text{O}_7^{2-}$ | 1.49 μM | 6 |
| 9 | $\text{In}(\text{H}_2\text{nha})_3$ | Turn-on | $\text{B}_4\text{O}_7^{2-}$ | 6.2 μM | This work |

Table S4 Various sensors for the detection of $\text{B}_4\text{O}_7^{2-}$.

| Fluorescent sensor | Sensing type | The detected anions | Ref |
|---|--------------|--|-----|
| 1 $\{[\text{Tb}(\text{dppa})(\text{H}_2\text{O})_2]\cdot\text{dima}\cdot\text{H}_2\text{O}\cdot0.5\text{O}\}_n$ | Turn-on | $\text{B}_4\text{O}_7^{2-}$, HSO_3^- , CO_3^{2-} , CH_3COO^- , HCO_3^- , $\text{S}_2\text{O}_3^{2-}$, I^- , S^{2-} , $\text{C}_2\text{O}_4^{2-}$, Br^- , Cl^- , SO_4^{2-} , NO_2^- , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ | 6 |
| 2 | Turn-on | F^- , Cl^- , Br^- , I^- , HSO_4^- , S^{2-} , SO_3^{2-} , SO_4^{2-} , CO_3^{2-} , HCO_3^- , CN^- , HPO_4^{2-} , H_2PO_4^- , $\text{P}_2\text{O}_7^{2-}$, $\text{B}_4\text{O}_7^{2-}$, CH_3COO^- , ClO_4^- | 7 |
| 3 | Turn-off | F^- , Cl^- , Br^- , I^- , HPO_4^{2-} , H_2PO_4^- , $\text{P}_2\text{O}_7^{4-}$, S^{2-} , CH_3COO^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , CN^- , ClO_4^- , $\text{B}_4\text{O}_7^{2-}$ | 8 |
| 4 | Turn-on | $\text{B}_4\text{O}_7^{2-}$, Cl^- , ClO_4^- , CN^- , CO_3^{2-} , H_2PO_4^- , HPO_4^{2-} , HS^- , I^- , NO_2^- , NO_3^- , CH_3COO^- , $\text{P}_2\text{O}_7^{4-}$, F^- , S^{2-} , Br^- , HCO_3^- | 9 |
| 5 | Turn-off | F^- , Cl^- , Br^- , I^- , ClO_4^- , S^{2-} , HS^- , SO_3^{2-} , $\text{S}_2\text{O}_8^{2-}$, CO_3^{2-} , SO_4^{2-} , HCO_3^- , CN^- , SCN^- , CH_3COO^- , Ppi , H_2PO_4^- , HPO_4^{2-} , NO_2^- , NO_3^- , $\text{B}_4\text{O}_7^{2-}$ | 10 |
| 6 | Turn-on | F^- , Cl^- , Br^- , I^- , ClO_4^- , H_2PO_4^- , CN^- , SiO_3^{2-} , CH_3COO^- , $\text{B}_4\text{O}_7^{2-}$, HS^- , S^{2-} , NO_3^- , CO_3^{2-} , HCO_3^- , HPO_4^- , $\text{P}_2\text{O}_7^{4-}$, NO_2^- | 11 |
| 7 | Turn-on | F^- , Cl^- , Br^- , I^- , HPO_4^- , H_2PO_4^- , $\text{P}_2\text{O}_7^{4-}$, S^{2-} , CH_3COO^- , CO_3^{2-} , HCO_3^- , CN^- , ClO_4^- , HS^- , NO_2^- , NO_3^- , $\text{B}_4\text{O}_7^{2-}$ | 12 |
| 8 | Turn-on | $\text{B}_4\text{O}_7^{2-}$, SO_4^{2-} , PO_4^{3-} , NO_3^- , NO_2^- , $\text{P}_2\text{O}_7^{2-}$, H_2PO_4^- , F^- , CH_3COO^- , Br^- , HCO_3^- | 13 |

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