Supporting Information

A Light-Operated Dual-Mode Method for Neuroblastoma Diagnosis Based on Tb-MOF : From Biometabolite Detection to Logic Devices

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Experimental Section

Materials and instruments: Reagents and characterization apparatus: Terbium nitrate was obtained by dissolving europium oxide in excess concentrated HNO_3 with continuous stirring and heating, followed by evaporation and crystallization several times. All other reagents and solvents were commercially available and used as received without further purification. The crystal structure of the as-prepared single crystal was analyzed using a Bruker SMART APEX II CCD area detector X-ray diffractometer, applying Mo Kα radiation (λ = 0. 71073 Å) at 50 kV and 30 mA. The structures were solved by direct methods and refined by full-matrix least-squares methods on all F^2 data (Olex2). Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. Crystal parameters and details of refinements are given in Table S1. The crystalline phases of the samples were determined by Powder X-ray diffraction patterns (PXRD) on a Bruker D8 diffractometer with Cu Kα radiation (40 kV, 40 mA) over the range of 4 ~ 50° at a scan rate of $0.1°·S^{-1}$. Simulation of the PXRD spectra was carried out by the single-crystal data and diffraction-crystal module of the Mercury programThermogravimetric analyses (TGA) were conducted on a PerkinElmer thermogravimetric analyzer from 30 to 600 °C at a rate of 10 °C·min^{-1} in flowing N_2. EDS mapping was observed on a Hitachi S-4800 scanning electron microscopy. Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet IS10 infrared spectrophotometer. X-ray photoelectron (XPS) spectra were recorded under ultrahigh vacuum ($<10^{-6}$ Pa) at a pass energy of 93.90 eV with an Axis Ultra DLD spectrometer (Kratos) by using a Mg Kα (1253.6 eV) anode. All binding energies were adjusted by using contaminant carbon (C 1s = 284.8 eV). The fluorescence spectra were examined on an Edinburgh FLS920 fluorescence spectrometer at room temperature. ^1H nuclear magnetic resonance (^1H NMR) spectra of the dissolved sample (diluted DCl and d-DMSO) were recorded on a Bruker Avance III 400. The UV-vis spectra of the VMA and Tb-DBA solutions were recorded on a Lambda 950 spectrophotometer. The corresponding Commission Internationale de I'Eclairage (CIE) color coordinates were calculated based on the international CIE standards.

Preparation of H₂DBA: A mixture of 9,10-dibromoanthracene (1.8 g, 5.4 mmol), 4-methoxycarbonylphenyl-boronic acid (2.92 g, 16.2 mmol), CsF (3 g, 19.7 mmol) and Pd(PPh₃)₄ (0.17 g, 0.15 mmol) was placed in a 150 mL two-necked shclenk flak and pumped for 15 min. 80 mL of degassed 1,2-dimethoxyethane was added through a canula. The mixture was heated to reflux under argon atmosphere for 60 h. After the mixture was cooled to room temperature, the solvent was removed. The yellow residue was suspended in water (40 mL) and extracted with CH₂Cl₂. After drying the mixed organic phase over MgSO₄ and removing the solvent, the crude product was purified by column chromatography (silica, CH₂Cl₂) to give the pure product of a yellow powder. 9,10-bis(p-(4-methoxycarbonyl)phenyl)anthracene (0.51 g, 1.15 mmol) was dissolved in 90 mL mixture of THF and MeOH (v/v = 2:1), 20 mL of a 20% KOH aqueous solution was added. The mixture was stirred to reflux for 12 h. The organic phase was removed under reduced pressure and the resulting suspension was diluted with 20 mL water. The precipitate formed by acidification with diluted hydrochloric acid was filtered and washed with water several times.
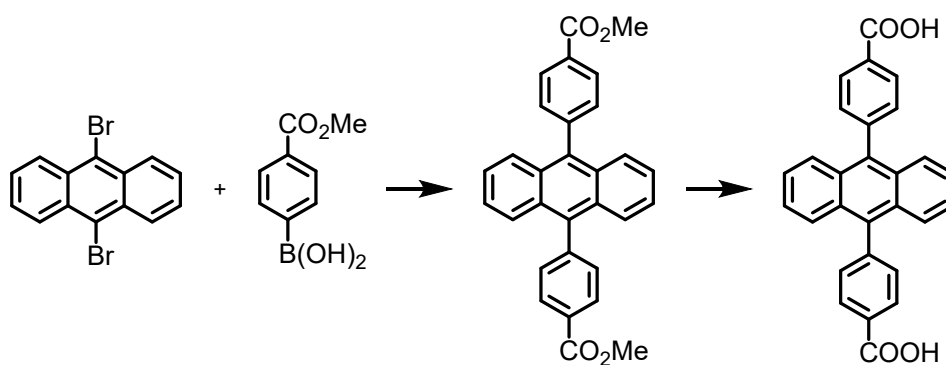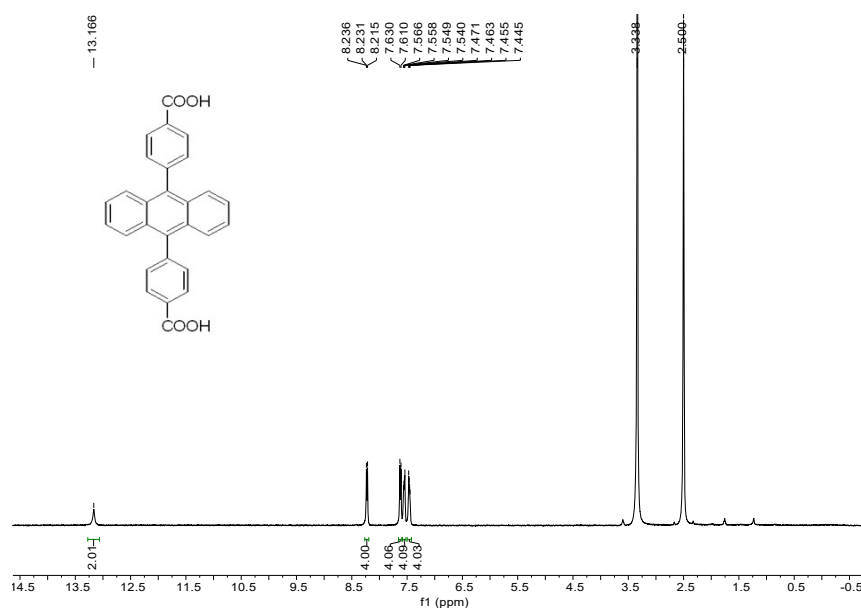
Fig. S1. ^{1}H NMR spectra of H$_2$DBA.

Preparation of Tb-DBA: 4,4′-(Anthracene-9,10-diyl)dibenzoic acid (H$_2$DBA) was synthesized by the Suzuki–Miyaura cross-coupling reaction of 9,10-dibromoanthracene and (4-(methoxycarbonyl)phenyl) boronic acid according to the reported methods. A mixture of H$_2$DBA (8 mg, 0.014 mmol) Tb(NO$_3$)$_3$·6H$_2$O (12mg, 0.026 mmol) and modulator 2-FBA (70 mg, 0.5 mmol) was dissolved in DMF (12 mL) in a screw cappedvial, then 100 μL HNO$_3$ (2.7 mol·L^{-1} in DMF) was added, the reactants were dispersed evenly by ultrasonic treatment for 3 min, and placed in an oven at 120 °C for 2 days. Yellow crystals with a rhombus shape were obtained after filtration. Yield: 53% based on Tb salt.

Procedures for VMA detection: In a typical assay for VMA using the sensory material, 1 mg of Tb-DBA ground powders were weighed and added to a 4.0 mL centrifuge tube containing the deionized water (3 mL) and a series of concentrations of fresh VMA aqueous solution (1-7×10^{-5} M, 3 mL), respectively, followed by ultrasonication to form the uniform dispersion. Then, the prepared suspensions were transferred to fluorescence cuvettes with covers, and their luminescence spectra were measured in the 400–650 nm range under excitations of both 360 and 286 nm. Test samples for the selectivity experiment were prepared with a similar procedure. Samples for specificity experiments were similarly prepared by adding Tb-DBA (1mg) into various aqueous solutions of biologically relevant species [NaCl, urea, glucose (Glu), creatinine (Crea),

NH$_4$Cl, KCl, Na$_2$SO4, creatine (Cre), 10^{-3} M]. The mixtures were then sonicated for luminescence measurements.

Procedures for EP Detection: Different concentrations of EP were dissolved in serum solution or aqueous solution and Tb-DBA (1mg) was added for uniform dispersion. Selective and anti-interference assays were prepared in a similar way. The different components contained in the serum (KCl, glucose(Glu), NaCl, L-proline(L-pro), MgCl$_2$, urea, NaHCO$_3$ and CaCl$_2$, 10^{-3} M). The prepared suspensions were transferred to fluorescence cuvettes with covers, and their luminescence spectra were measured in the 400–650 nm range under excitation at 360 nm.

Serum and artificial urine sample preparation: The goat serum and artificial urine samples were prepared using the reported procedures.

Table S1. Crystal data and refinement parameters for **Tb-DBA**.

Identification code	Tb-DBA
Chemical formula	C$_{124}$H$_{92}$N$_4$O$_{20}$Tb$_3$
Formula weight	2434.77
Crystal Colour	Yellow
Temperature (K)	100(2)
Crystal System	Monoclinic
Space Group	$P2(1)/c$
a (Å)	13.4193
b (Å)	36.0272
c (Å)	13.341
α(°)	90
β(°)	118.876
γ(°)	90
Z	2
V(Å^3)	5467.9(4)
D$_{calc}$ (g cm^{-3})	1.432
F(000)	2438
Mu (mm^{-1})	1.927
R (int)	0.0473
Number of parameters	767
GOF on F^2	1.044
$R1^a$[I>2δ(I)]	0.0832
wR_2^b(all data)	0.2290
CCDC	2212905

$R_1 =\Sigma(||F$o$| - |F$c$||)/\Sigma|F$o$|$; w$R_2 =\{\Sigma w(|F$o$|^2 -|F$c$|^2)^2/\Sigma w(|F$o$|^2)^2\}^{1/2}$.
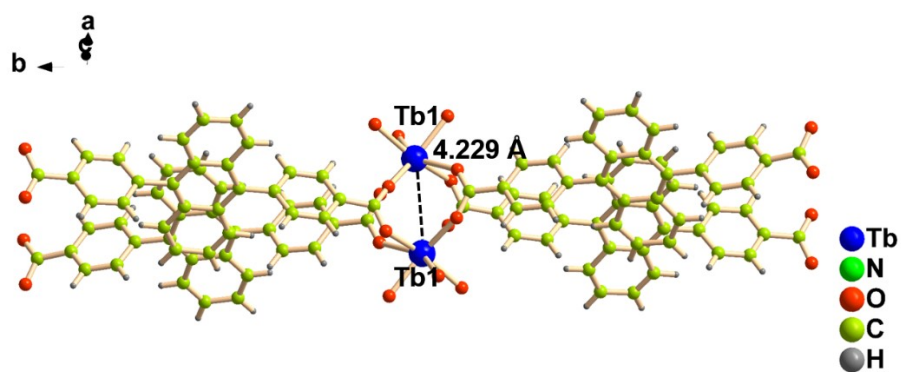
Fig. S2. The coordination configuration of the two adjacent Tb(1) centre in Tb-DBA.
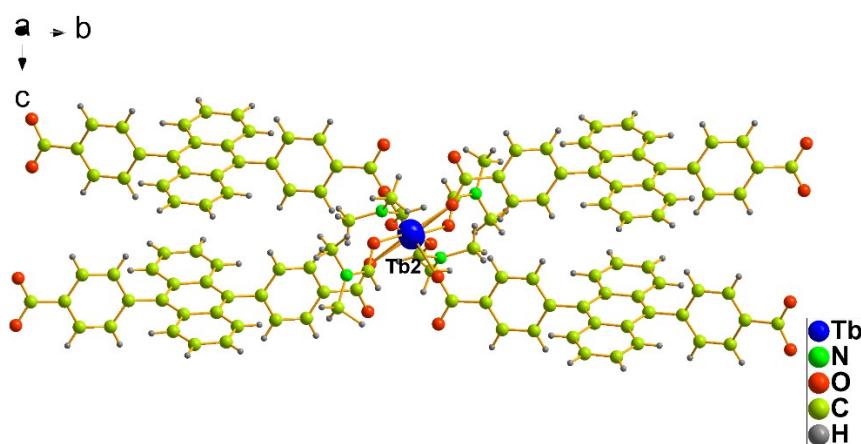

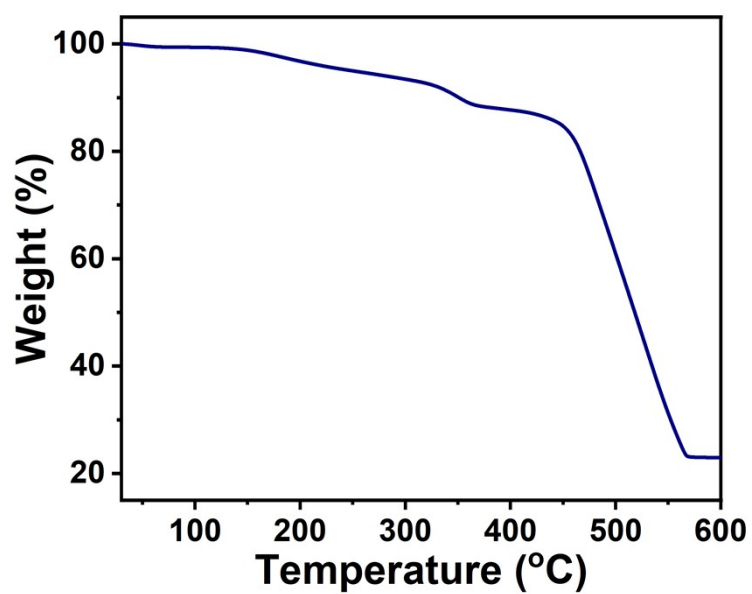**Fig. S3.** The coordination configuration of the Tb(2) in Tb-DBA.

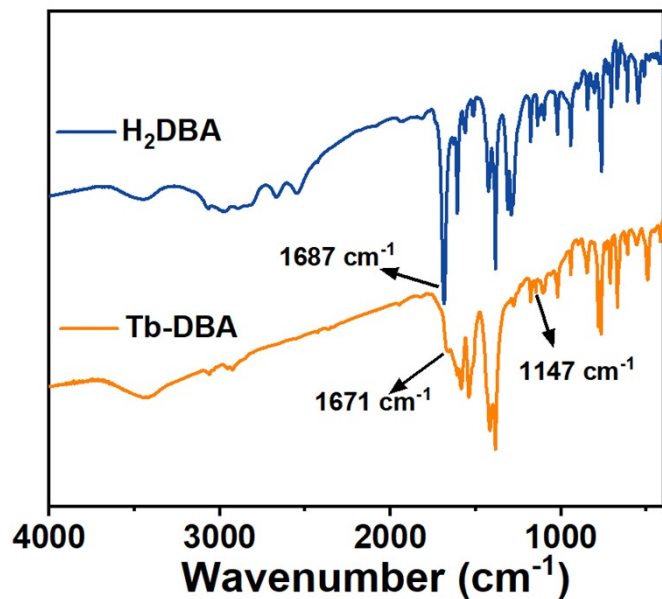**Fig. S4.** TGA traces of Tb-DBA ranging from room temperature to 600 °C.

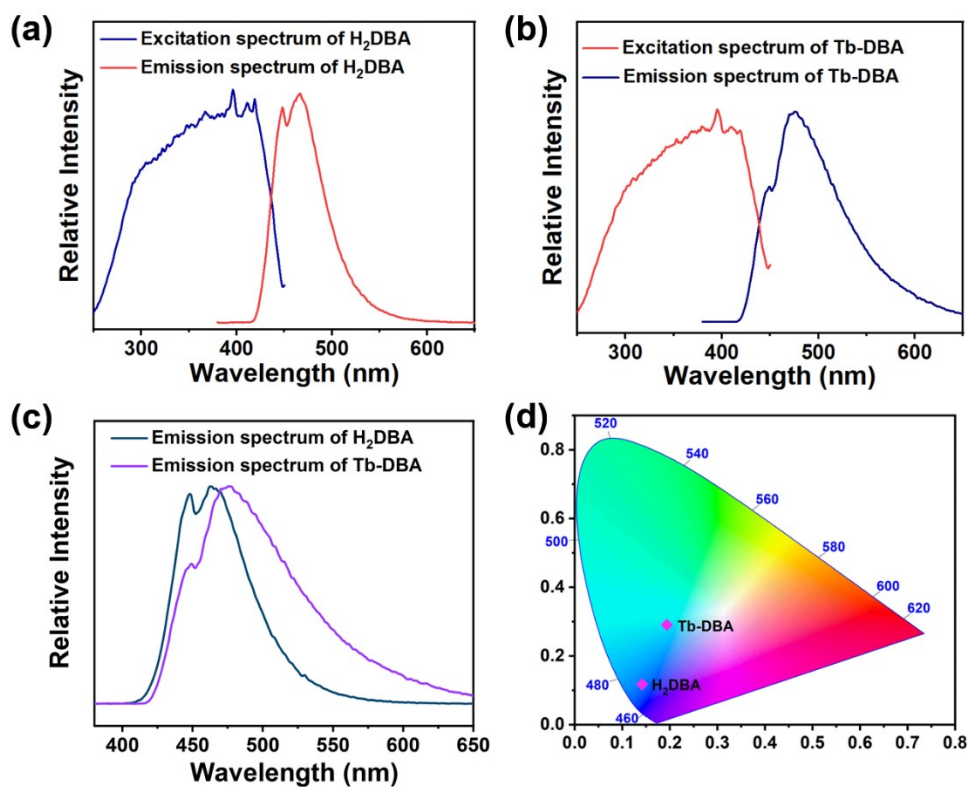**Fig. S5.** FT-IR spectra of H_2DBA (blue), Tb-DBA (yellow).

Fig. S6. (a-b) The excitation and emission spectra of H_2DBA and Tb-DBA in solid state. (c-d) Emission spectra and CIE chromaticity coordinates of H_2DBA and Tb-DBA in solid state.
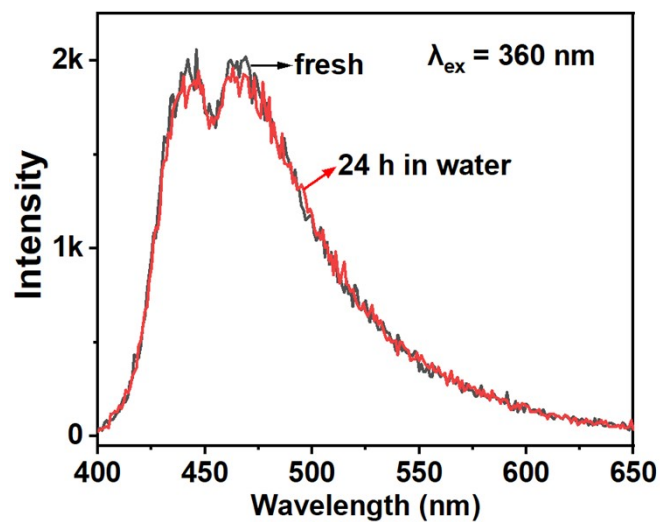
Fig. S7. luminescence spectra (λex = 360 nm) of Tb-DBA in water solution before and after storage in water for 24 h.
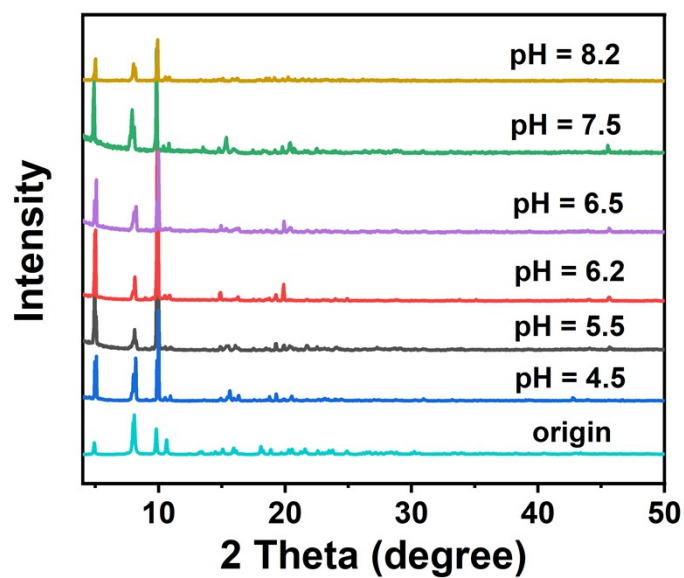
Fig. S8. PXRD patterns of Tb-DBA after immersion in pH = 4.5–8.2 solutions for 24 h.
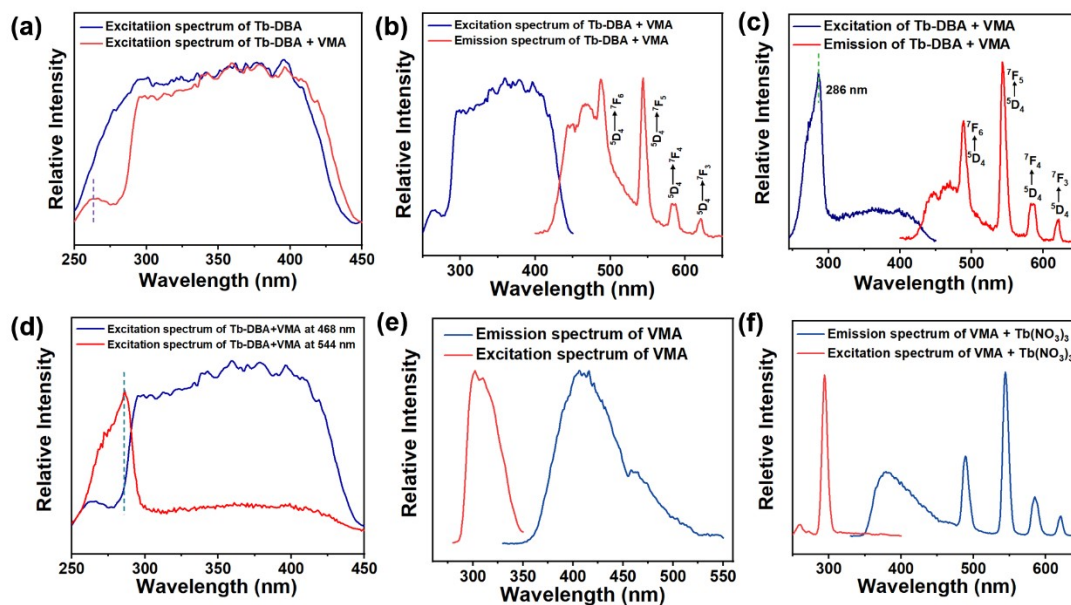
Fig. S9. (a) The excitation spectra of Tb-DBA and Tb-DBA+VMA (λ_{em} = 468 nm); (b) The excitation spectra of Tb-DBA+VMA (λ_{em} = 468 nm) and emission spectra of it (λ_{ex} = 264 nm); (c) The excitation spectra of Tb-DBA+VMA (λ_{em} = 544 nm) and emission spectra of it (λ_{ex} = 286 nm); (d)The excitation spectra of Tb-DBA+VMA at 468 nm and 544 nm emission, respectively; (e) The excitation and emission spectra of VMA; (f) The excitation and emission spectra of VMA in Tb(NO$_3$)$_3$ solution.
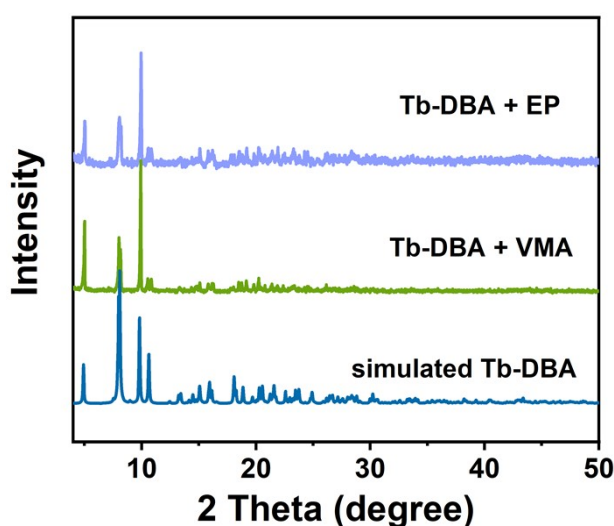
Fig. S10. PXRD patterns of HOF-DBA and after sensing VMA (green) and EP (purple).
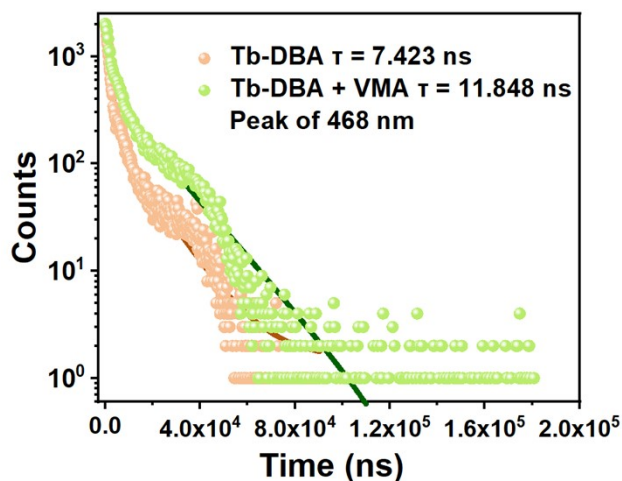
Fig. S11. Decay lifetimes of 468 nm emission peak for Tb-DBA and Tb-DBA+VMA (C = 10^{-4} M) (λex = 360 nm).
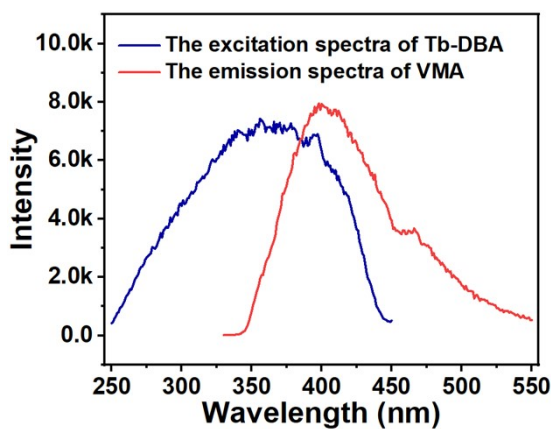
Fig. S12. The excitation spectra of Tb-DBA and the emission spectra of VMA.
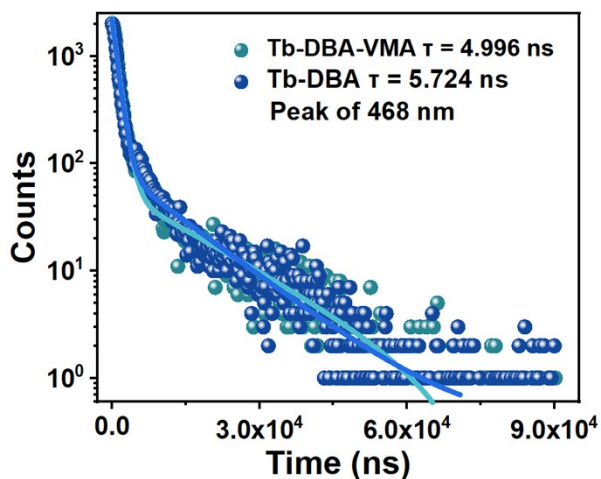

Fig. S13. Decay lifetimes of 468 nm emission peak for Tb-DBA and Tb-DBA+VMA (C = 10^{-4} M) (λex = 286 nm).
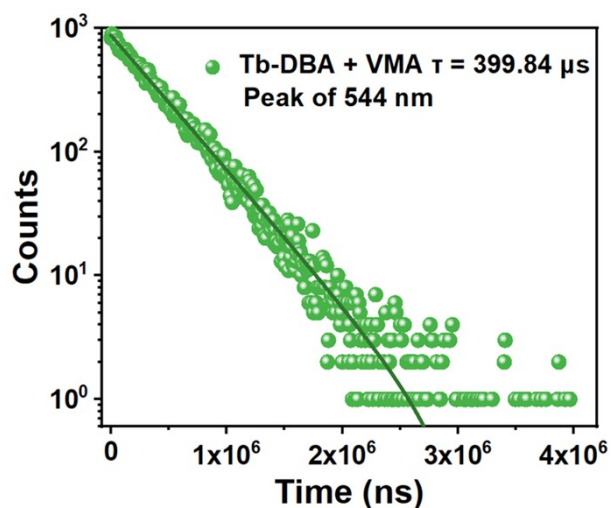
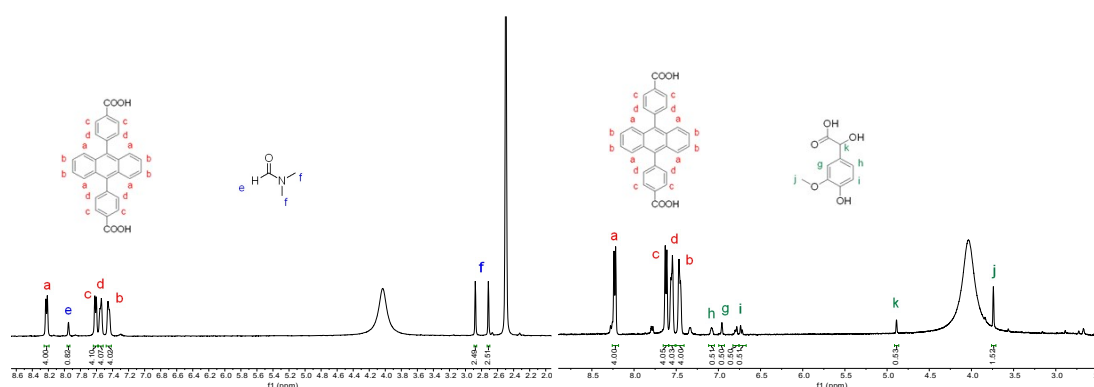**Fig. S14.** Decay lifetime of 544 nm emission peak for Tb-DBA+VMA (C = 10⁻⁴ M) (*λex* = 286 nm).

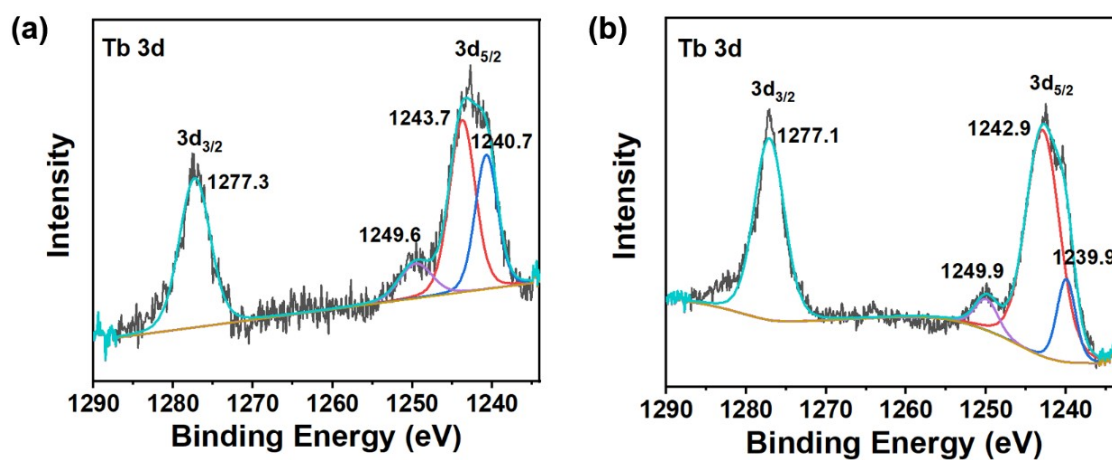**Fig. S15.** ¹H NMR spectra of Tb-DBA and Tb-DBA+VMA.

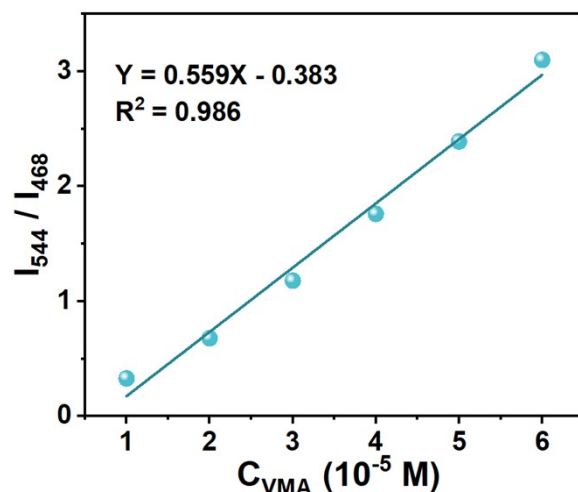**Fig. S16.** (a) XPS spectrum of Tb 3d electrons in Tb-DBA and Tb-DBA+VMA(b).

Fig. S17. Calibration curves of Tb-DBA added VMA in aqueous solution with different concentrations (1-6 – 10^{-5} M).
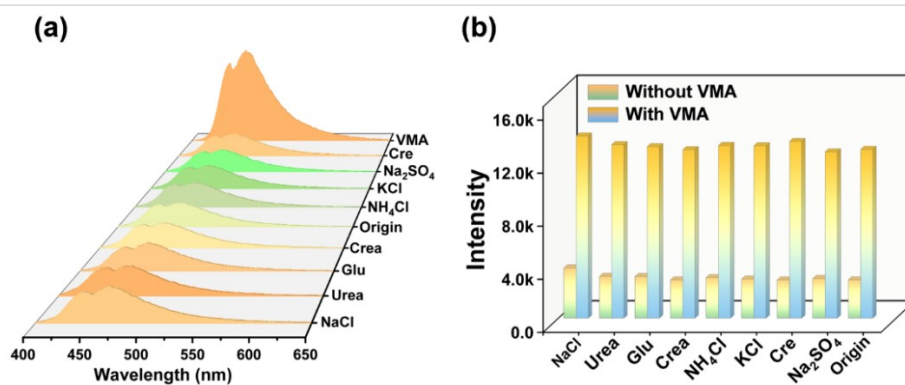

Fig. S18. (a) The emission spectra of Tb-DBA in VMA and various components (10^{-3} M) in urine system. (b) Corresponding intensity at 468 nm for Tb-DBA toward various components in urine system.
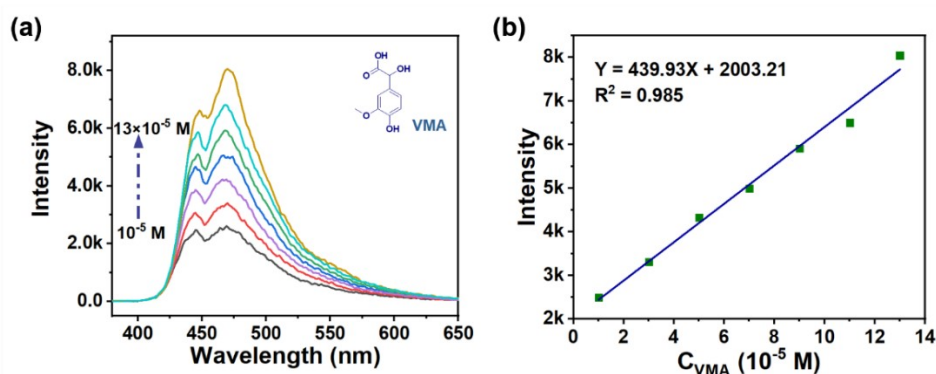

Fig. S19. (a) The emission spectrums ($\lambda ex = 360$ nm) of Tb-DBA immersed in various concentration of VMA in urine ($1-13\times10^{-5}$ M). (b) Dependence of emission intensity of Tb-DBA on concentration of VMA in urine.
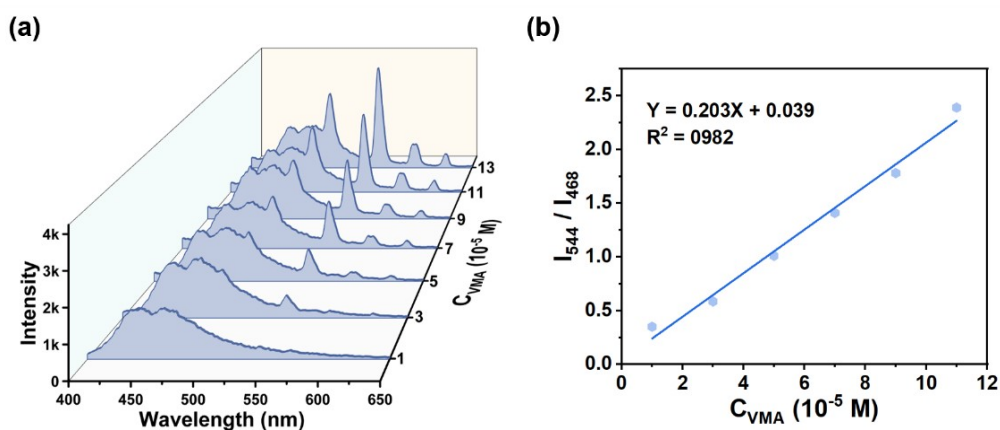
Fig. S20. (a) The emission spectrums (λex = 286 nm) of Tb-DBA immersed in various concentration of VMA in urine ($1-13\times10^{-5}$ M). (b) Linear relationship between the concentration of VMA ($1-11\times10^{-5}$ M) and the variation of the ratio under the single excitation of 286 nm.
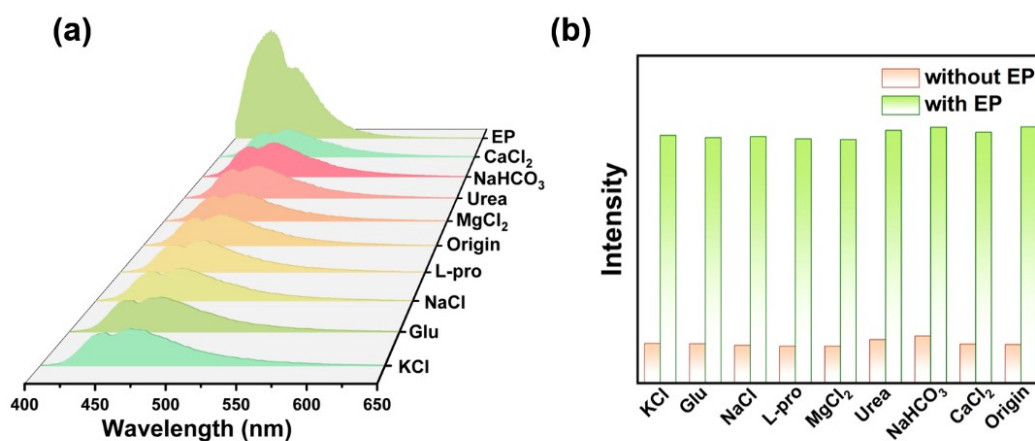

Fig. S21. (a) The emission spectra of Tb-DBA in EP and various components (10^{-3} M) in urine system. (b) Corresponding intensity at 435 nm for Tb-DBA toward various components in serum system.
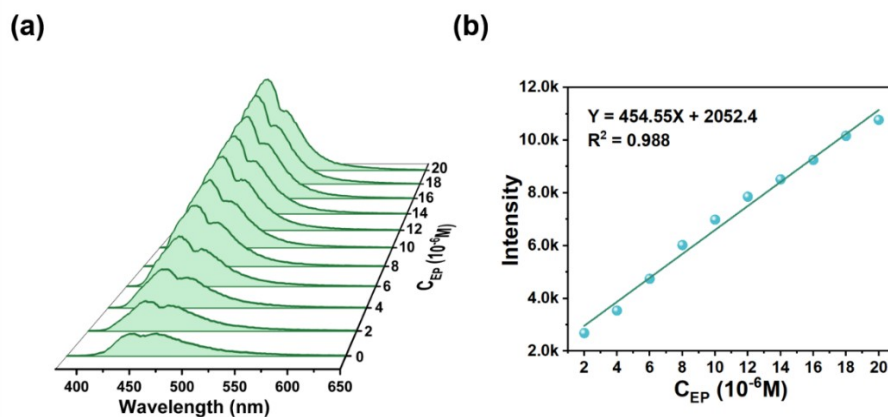
Fig. S22. (a) The emission spectrums (λex = 360 nm) of Tb-DBA immersed in various concentration of EP in serum (0−20×10⁻⁵ M). (b) Dependence of emission intensity of Tb-DBA on concentration of VMA in serum.
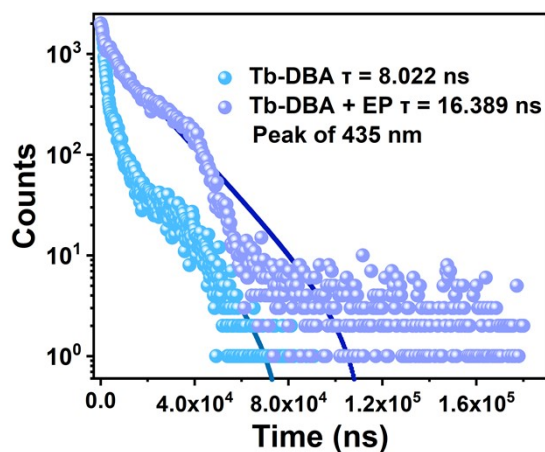

Fig. 23. RTP decay lifetime of the 435 nm emission peak for Tb-DBA and Tb-DBA + EP.
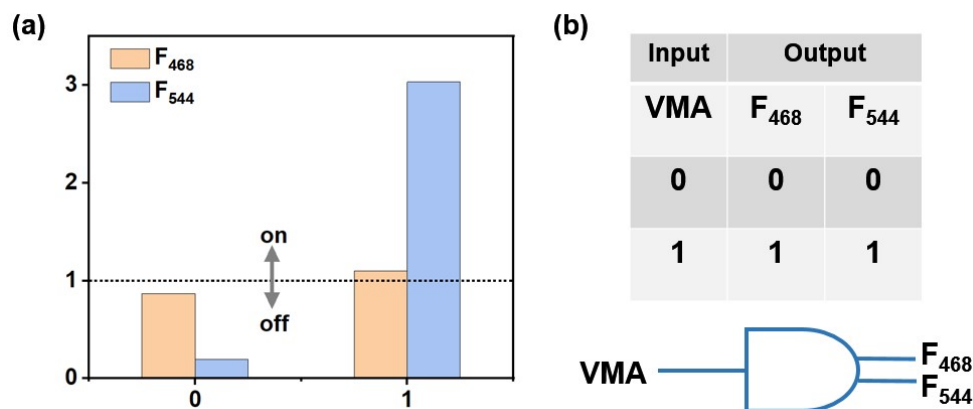

Fig. 24. (a) Column diagram of the normalized fluorescence intensity of F_{468} and F_{544} toward VMA (7 × 10⁻⁵ M). (b) Truth table of the one-to-two decoder logic gate.

Table S2. Summary of decay lifetime of Tb-DBA, Tb-DBA-VMA, and Tb-DBA-EP.

Sample	λ_{ex} (nm)	λ_{em} (nm)	T_1 (ns)	A_1	Percentage (%)	T_2 (ns)	A_2	Percentage (%)	T^* (ns)	R^2
Tb-DBA	360	468	1.56	1844.98	48.72	13.11	231.27	51.28	7.42	0.986
Tb-DBA-VMA	360	468	2.29	1632.69	31.93	16.99	469.42	68.07	11.84	0.991
Tb-DBA	360	435	1.74	2078.41	58.44	16.86	152.57	41.56	8.02	0.982
Tb-DBA-EP	360	435	1.61	823.42	6.07	17.34	1182.4	93.93	16.39	0.998
Tb-DBA	286	468	1.19	2208.28	72.07	17.63	57.75	27.93	5.72	0.996
Tb-DBA-VMA	286	468	1.11	2108.83	66.61	12.73	92.16	33.39	4.99	0.992

$[\tau^* = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)]$