ESI

A heterobimetallic metal-organic framework as "turn-on" sensor

toward DMF

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1. Experimental section

Materials and Methods

HPBA was synthesized prepared according to the previous reports.¹⁻³. All other reagents and solvents were obtained from commercial sources and used as received.

Elemental analyses for C, H and N in the solid sample were carried out on a VarioEL analyzer. The infrared (IR) spectra (diamond) were recorded on a Nicolet 7600 FT-IR spectrometer within the 4000-500 cm⁻¹ region. TGA (thermal gravimetric analysis) was recorded under an air atmosphere with a heating rate of 10 °C/min using a a SDT 2960 Simultaneous DSC-TGA of TA instrument in the temperature range of 50-800 °C. Powder X-ray power diffraction (PXRD) patterns were collected by a D8 Focus (Bruker) diffractometer with Cu K α radiation Field-emission ($\lambda = 0.15405$ nm). The photoluminescence (PL) excitation and emission spectra were performed on a Hitachi F-7000 spectrophotometer equipped with a 150W xenon lamp as the excitation source at room temperature. All ICP tests are performed on a ICP-OES (ICP 6300, Thermo Scientific, USA) instrument based on solid samples for NBU-8 after treatment of DMF and CH₃CN solvents for ten days.

Synthesis of {Eu₂Cu₃(PBA)₆(NO₃)₆•H₂O}_n (NBU-8)

Eu(NO₃)₃•6H₂O (0.1 mmol, 44.6 mg), Cu(NO₃)₂•3H₂O (0.1 mmol, 24.2 mg), and HPBA (0.5 mmol, 100.1 mg) in a mixed solvent of acetonitrile (CH₃CN, 6 ml) and distilled water (H₂O, 1 ml) were placed in a Teflon-lined stainless steel vessel (20 mL) and heated to 80 °C in 300 min, maintained at this temperature for three days and then cooled to room-temperature at a rate of 0.5 °C/min. The resulting blue crystals were obtained, after being washed by distilled water, yield ~69.3 mg (68% based on Cu²⁺). Its purity was confirmed by powder X-ray diffraction (Fig. S3). Elemental analysis (calc %) for **NBU-8** C₆₆H₄₄Cu₃Eu₂N₁₈O₃₁ (*M*r = 2079.73): C, 38.12; H, 2.13; N, 12.12. Found: C, 38.23; H, 2.15; N, 12.04. Selected IR peaks (cm⁻¹) for **NBU-8**: 3427 (m), 3081 (w), 2502 (w), 2424 (w), 2w), 1983 (w), 1780 (w), 1739 (w), 1591 (s), 1542 (s), 1477 (s), 1440 (w), 1416 (vs), 1382 (m), 1346 (w), 1293 (vs), 1185 (m), 1115 (w), 1054 (w), 1033 (m), 1013 (w), 926 (w), 862 (m), 811 (w), 780 (m), 744 (w), 719 (m), 685 (w), 655 (m), 578 (w), 552 (w).

X-ray crystal structure determination:

Diffraction intensity data for single crystal of NBU-8 was collected at 293 K on a

Bruker Apex II CCD diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Data processing was accomplished with the SAINT program. Absorption corrections were applied using SADABS.⁴ The structure was solved by direct methods using SHELXS-97 program of the SHELXTL package and refined by using the full-matrix least squares method on F^2 with SHELXTL-97.⁵ Anisotropic displacement parameters were applied to all non-hydrogen atoms. Hydrogen atoms were located geometrically and were added to the structure factor calculation. The formula for **NBU-8** was determined by combining single-crystal structure, elemental microanalysis and TGA. A summary of the crystallographic data for complex **NBU-8** is listed in Table S1. Selected bond lengths and angles are shown in Table S2. CCDC-1561729 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Fluorescence measurements

The luminescent properties of **NBU-8** were examined in the solid state, in organic solvent suspensions at room temperature. The photoluminescence (PL) excitation and emission spectra were recorded on a Hitachi F-7000 spectro photometer equipped with a 150 W xenon lamp as the excitation source. Prior to the measurements, some preparatory work was done. Crystals of **NBU-8** were ground into powder and used for luminescent experiments in solutions.

NBU-8 (5 mg) was placed into a centrifuge tube with different solvents (3 mL), including acetone, dichloromethane (CH₂Cl₂), trichloromethane (CHCl₃), N,N'-dimethylformamide (DMF), N,N'-dimethyl acetamide (DMA), 1,4-dioxane, ethyl acetate (EA), ethanol (EtOH), methanol (MeOH), tetrahydrofuran (THF), hexane, acetonitrile (CH₃CN), formamide (FA), acetamide (AA), propionamide (PA), urea, N,N'-diethylformamide (DEF), benzamide (BA) formic acid (HCOOH), acetic acid (CH₃COOH), propanal, benzal dehyde, 1-Methyl-2-pyrrolidinone (NMP), and nitromethane. Subsequently the sample tube was taken out and quickly sealed, then the emission spectra were recorded.

In-situ time-dependent luminescent experiments were prepared, as follows. Solid samples of **NBU-8** (3 mg) were added into a testing quartz cuvette with DMF of 3 mL, and the cap is carefully put on the cuvette. Then the luminescence spectra and intensity of **NBU-8** as a sensor versus time plots were obtained in DMF solvent. So do **NBU-8** with different particle sizes.

For concentration-dependent luminescence measurements were prepared, as follows. Different amounts of DMF were added into a standard **NBU-8** emulsion in CH₃CN, while the concentration of **NBU-8** was kept constant. The PL spectra of the solvent@**NBU-8** emulsions were treated by ultrasonication for 10 min and then aged for 24 hours to form stable emulsion before fluorescence study.

Structure description:

As shown in Fig. 1a, its asymmetric unit consists of one third crystallographically independent Eu^{3+} ion, one half Cu^{2+} ion, one nitrate anion,

one deprotonated {PBA}- anion and one free water molecule. Eu1 is located at 3-fold axis and coordination with three carboxylate oxygen atoms from three {PBA}⁻ ligands, six oxygen atoms from three nitrate groups, forming a slightly distorted tricapped trigonal prism (Fig. S1a), in which three carboxylate oxygen atoms (O1) and three nitrate oxygen atoms (O4) from three nitrate anions occupy the points of the trigonal prism, another three nitrate oxygen atoms (O3) locating the tricapped positions. Cu1 lies on 2-fold axis. The result (1.92) of bond valence sum (BVS) calculation verify that the Cu²⁺ center is octahedral coordination containing two much longer Cu-O3 bonds of 2.580(3) in the axis positions with 9.12% contribution, the other two Cu-O2 and Cu-N1 bond lengths are 1.945(2) Å and 2.035(3) Å (Table S2), occupying plane positions. The {PBA}⁻ ligand acts as a μ_3 -bridge, in which one bidentate carboxylate group connect one Cu center and one Eu center via two unidentate carboxylate oxygen atoms, the pyrimidine group connects one Cu center through one unidentate N1 atom with one open N2-site. As shown in Fig. S1b, Eu1 center is connected to six Cu²⁺ centers by three carboxylate groups and three N-atoms from three $\{PBA\}^{-}$ ligands along *c*-axis, in which three coordinated nitrate groups are omitted for clarify because they do not participate in the construction of target framework. Furthermore, the six Cu²⁺ centers are bridged to nine Eu^{3+} centers by carboxylate groups of {PBA}⁻ ligands (Fig. S1c), forming to target three dimensional network along [001] direction (Fig. 1b and S1d). The overall structure can be simplified into a 3,3,4-connected 3-nodal T10 net with a point symbol of $\{8^3\}_8\{8^6\}_3$ by freely available computer program TOPOS (Fig. S1e). From another perspective, the 3D framework of NBU-8 can be also considered that Cu centers are bridged by cis-connected two oxygen atoms (O2) and two N atoms (N1) from four {PBA}⁻ ligands (Fig. S2a) into a 3D network, labeled as Cu-PBA 3D net, with a cylindrical channel of ~ 7 $Å \times 7 Å$ (a/2) along *c*-axis (Fig. S2b). The leaving carboxylate oxygen atoms (O1) point to the interior of hole, coordinating Eu centers (Fig. S2d). In other words, Eu³⁺ ions do not make a contribution to construction of the final 3D skeleton. Therefore, if all Eu ions and nitrate groups are omitted, the 3D framework of Cu-PBA (Fig. S2b) can be regarded as a (2,4)-connected 2-nodal network (Fig. S2c) with its point symbol of $\{12^4.16^2\}\{12\}_2$, in which $\{PBA\}^$ ligands became bidentate nodes, furthermore being simplified as a 4-connected uninodal NbO net with the point symbol of $\{6^4, 8^2\}$ if bidentate nodes were transformed into linked bonds (Fig. S2d). Hence Eu centers can be also viewed as incorporating into the one-dimensional (1D) channels in Cu-PBA 3D framework along *c*-axis by coordination. The phase purity of NBU-8 bulk sample was confirmed by powder XRD with identical peaks between assynthesized sample and simulated data (Fig. S3a).

Table S1 Summary of Crystal Data and Structure Results for NBU-8.

CCDC	1561729		
Empirical formula	$C_{66}H_{44}Cu_{3}Eu_{2}N_{18}O_{31}$		
structural formula	${Eu_2Cu_3(PBA)_6(NO_3)_6 \bullet H_2O}_n (NBU-8)$		
fw	2079.73		
Crystal system	trigonal		
Space group	<i>R</i> -3c		
Temperature (K)	296(2)		
Λ (Mo Kα), Å	0.71073		
<i>a</i> / Å	14.0021(3)		
b / Å	14.0021(3)		
<i>c</i> / Å	63.523(3)		
lpha / °	90		
eta / °	90		
γ / °	120		
<i>V</i> / Å ³	10785.7(5)		
Ζ	6		
$2\theta \max (\deg)$	52.14		
μ (Mo-K α) mm ⁻¹	2.697		
D, g/cm ³	1.921		
F(000)	6162		
Crystal size (mm ³)	0.25×0.23×0.20		
Reflections collected / unique	$21300/2373 [R_{int} = 0.0472]$		
Final <i>R</i> indices $[I > 2\sigma(I)]$	${}^{a}R_{1} = 0.0296,$		
<i>R</i> indices (all data)	${}^{b} wR_{2} = 0.0856$ ${}^{a} R_{1} = 0.0377,$ ${}^{b} wR_{2} = 0.0912$		
GOF	1.075		

 ${}^{a}\overline{R_{1} = \Sigma ||F_{o}| - |F_{c}||/a|F_{o}|, {}^{b}wR_{2} = \{\Sigma w[(F_{o})^{2} - (F_{c})^{2}]^{2}/\Sigma w[(F_{o})^{2}]^{2}\}^{1/2}}$

Table S2. Selected bond lengths and bond angles for NBU-8.

Eu(1)-O(1)	2.312(3)	Eu(1)-O(1)#1	2.312(3)
Eu(1)-O(1)#2	2.312(3)	Eu(1)-O(3)	2.518(3)
Eu(1)-O(3)#1	2.518(3)	Eu(1)-O(3)#2	2.518(3)
Eu(1)-O(4)	2.469(3)	Eu(1)-O(4)#1	2.469(3)
Eu(1)-O(4)#2	2.469(3)	Eu(1)-N(3)	2.927(3)
Eu(1)-N(3)#1	2.927(3)	Eu(1)-N(3)#2	2.927(3)
Cu(1)-O(2)#3	1.945(2)	Cu(1)-O(2)#4	1.945(2)
Cu(1)-N(1)	2.035(3)	Cu(1)-N(1)#5	2.035(3)
Cu(1)-O(3)#6	2.580(3)	Cu(1)-O(3)#7	2.580(3)
O(2)-Cu(1)#8	1.945(2)		
O(1)#1-Eu(1)-O(1)	85.90(11)	O(1)#1-Eu(1)-O(1)#2	85.90(11)
O(1)#2-Eu(1)-O(1)	85.90(11)	O(1)#1-Eu(1)-O(4)#1	146.86(10)
O(1)-Eu(1)-O(4)#1	84.92(10)	O(1)#2-Eu(1)-O(4)#1	124.99(9)
O(1)#1-Eu(1)-O(4)#2	84.92(10)	O(1)#2-Eu(1)-O(4)#2	146.86(10)
O(1)-Eu(1)-O(4)#2	124.99(9)	O(1)#1-Eu(1)-O(4)	125.00(9)
O(1)#1-Eu(1)-O(3)#1	152.62(10)	O(1)#2-Eu(1)-O(3)#1	74.13(9)
O(1)#1-Eu(1)-N(3)#1	162.42(10)	O(1)#2-Eu(1)-N(3)#1	99.78(10)
O(1)-Eu(1)-N(3)#1	78.00(11)	O(1)#1-Eu(1)-N(3)	99.78(10)
O(1)#2-Eu(1)-N(3)	78.00(11)	O(1)-Eu(1)-N(3)	162.42(10)
O(1)#1-Eu(1)-N(3)#2	77.99(11)	O(1)#2-Eu(1)-N(3)#2	162.42(10)
O(1)-Eu(1)-O(3)#1	74.35(10)	O(1)-Eu(1)-N(3)#2	99.78(10)
O(1)-Eu(1)-O(4)	146.86(10)	O(1)#2-Eu(1)-O(4)	84.92(11)
O(1)#1-Eu(1)-O(3)	74.13(9)	O(1)#2-Eu(1)-O(3)	74.35(10)
O(1)-Eu(1)-O(3)	152.61(10)	O(1)#1-Eu(1)-O(3)#2	74.35(10)
O(1)#2-Eu(1)-O(3)#2	152.62(10)	O(1)-Eu(1)-O(3)#2	74.13(9)
O(3)-Eu(1)-N(3)#1	123.38(9)	O(3)-Eu(1)-N(3)	25.74(9)
O(3)-Eu(1)-O(3)#1	116.62(4)	O(3)-Eu(1)-O(3)#2	116.62(4)
O(3)-Eu(1)-N(3)#2	94.28(10)	O(3)#1-Eu(1)-N(3)#2	123.38(9)
O(3)#1-Eu(1)-N(3)#1	25.74(9)	O(3)#1-Eu(1)-N(3)	94.27(10)
O(3)#2-Eu(1)-N(3)#1	94.27(10)	O(3)#2-Eu(1)-O(3)#1	116.61(4)
O(3)#2-Eu(1)-N(3)#2	25.74(9)	O(3)#2-Eu(1)-N(3)	123.38(9)
O(4)-Eu(1)-O(3)	51.18(9)	O(4)-Eu(1)-N(3)#2	98.49(10)
O(4)-Eu(1)-O(3)#2	121.90(10)	O(4)-Eu(1)-O(3)#1	72.51(9)
O(4)-Eu(1)-N(3)#1	72.33(9)	O(4)-Eu(1)-N(3)	25.45(9)
O(4)#1-Eu(1)-O(4)#2	74.64(11)	O(4)#1-Eu(1)-O(4)	74.64(11)
O(4)#1-Eu(1)-O(3)	121.91(10)	O(4)#1-Eu(1)-O(3)#2	72.51(9)
O(4)#1-Eu(1)-O(3)#1	51.18(9)	O(4)#1-Eu(1)-N(3)#1	25.45(9)
O(4)#1-Eu(1)-N(3)	98.49(10)	O(4)#1-Eu(1)-N(3)#2	72.33(9)
O(4)#2-Eu(1)-O(3)	72.51(9)	O(4)#2-Eu(1)-O(4)	74.64(11)
O(4)#2-Eu(1)-O(3)#2	51.18(9)	O(4)#2-Eu(1)-O(3)#1	121.91(10)
O(4)#2-Eu(1)-N(3)	72.33(9)	O(4)#2-Eu(1)-N(3)#2	25.45(9)
O(4)#2-Eu(1)-N(3)#1	98.49(10)	N(3)-Eu(1)-N(3)#2	97.68(9)
N(3)#1-Eu(1)-N(3)	97.68(9)	N(3)#1-Eu(1)-N(3)#2	97.68(9)

O(2)#3-Cu(1)-O(2)#4	96.56(15)	O(2)#3-Cu(1)-N(1)	166.84(11)
O(2)#3-Cu(1)-N(1)#5	88.14(11)	O(2)#3-Cu(1)-O(3)#7	82.50(10)
O(2)#4-Cu(1)-N(1)#5	166.84(11)	O(2)#4-Cu(1)-N(1)	88.14(11)
O(2)#3-Cu(1)-O(3)#6	100.65(10)	O(2)#4-Cu(1)-O(3)#7	100.65(10)
O(2)#4-Cu(1)-O(3)#6	82.50(10)	O(3)#6-Cu(1)-O(3)#7	175.33(13)
N(1)-Cu(1)-N(1)#5	89.98(16)	N(1)-Cu(1)-O(3)#6	92.13(10)
N(1)-Cu(1)-O(3)#7	84.56(10)	N(1)#5-Cu(1)-O(3)#6	84.56(10)
N(1)#5-Cu(1)-O(3)#7	92.13(10)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+y+2, -x+1, z; #2 -y+1, x-y-1, z; #3 -y+4/3, -x+5/3, z+1/6; #4 y+2/3, -x+y+4/3, -z+1/3; #5 - x+2, -x+y+1, -z+1/2; #6 -x+y+7/3, y+2/3, z+1/6; #7 x-y-1/3, x-2/3, -z+1/3; #8 x-y+2/3, x-2/3, -z+1/3.



(a)







Fig. S1 (a) The polyhedra of Eu. Symmetry code for the generated atoms: A -x+y+2, -x+1, z; B -y+1, x-y-1, z. (b, c and d) The connected mode of Eu and Cu ions in **NBU-8** as well as the detailedly formed procedure of 3D framework for **NBU-8** along *c*-axis from (b) to (c) and (d). (e) The simplified (3,3,4)-net of **NBU-8**. Eu-PBA bond and Cu-PBA bonds are labeled as yellow and blue lines, respectively.





Fig. S2 Analyze the formed procedure of 3D framework of NBU-8 from another point of view. (a)

The connected mode of Cu-PBA. (b) The formed 3D network of Cu-PBA, in which Cu, C, N, O are labeled as turquiose, yellow, blue and red balls, Cu-N and Cu-O bonds are drawn as blue lines, other bonds are drawn as yellow lines. (c) The simplified (2,4)-connected net along *c*-axis, in which Cu atoms and $\{PBA\}^-$ ligands are drawn as blue and yellow balls, Cu-PBA bonds are drawn as yellow lines. (d) The simplified 4-connected *NbO* net along *c*-axis, in which Cu atoms are drawn as violet balls, 2-connected PBA ligands are drawn as bridged bonds.



Fig. S3 (a) Simulated and measured XRD powder patterns for compound **NBU-8**. (b and c) The PXRD patterns for **NBU-8** samples after being immersed into various organic solvents. (d) The PXRD pattern for **NBU-8** sample after 2 months in air atmosphere.



Fig. S4 The TGA and DSC curves of compound NBU-8

The TGA curve of compound **NBU-8** under air atmosphere with a heating rate of 10 °C/ min was investigated in the temperature range of 25-700 °C, as shown in Fig. S4. The TGA curve shows three main weight losses. A minor weight loss occured at 255 °C, corresponding to the loss of one free water molecule (found, 0.89%; cald. 0.87%). Then dehydrated framework is stable to 315 °C, then the framework begins to collapse and exhibits two continuous weight losses, accompanying the release of organic ligands (HPBA) and nitrate complex anions. The total weight loss at 447 °C is 69.1%. The final residual for compound **NBU-8** was not characterized due to the its corrosive reactions with the TGA buckets made of Al₂O₃, however it is expected to be main europium(III) oxide and copper(II) oxide (found, 69.1%; cald. 71.6%).





Fig. S5 Solid state excitation and emission spectra of free HPBA ligand (a) and compound **NBU-8** (b) at room temperature. (c) The solid-state photoluminescence spectrum of **NBU-8** after immersing in DMF solvent for 3 days.

As were demonstrated in reported literature,^{8c,d,9} Cu²⁺ ion is typical luminescent quencher due to electron transfer or excited-state electron transfer mechanism. In these literature, luminescent materials exhibit significant luminescence quenching in the presence of Cu²⁺ solution. Take lanthanide compound as an example in Ref. 9c,d,e, the interaction between Cu²⁺ ion and organic ligand minimizes the energy transfer efficiency from the ligands to the lanthanide center, thus decreasing the luminescent intensity, even quenching after lanthanide compound was immersed into the solution with Cu²⁺ ions. Based on the above consideration, we synthesized directly a heterobimetallic MOF (NBU-8) based on Cu²⁺ and Eu³⁺ ions in this work. The NBU-8 will be non-luminescent, which has been demonstrated by solid-state luminescent result of NBU-8, since the interaction between compounds and inserted Cu²⁺ ions. Combining the structural feature of NBU-8 in Fig. 1a and Fig. S1, the Cu centers coordinate with N-sites from pyrimidine and O-sites from carboxylate groups, and Eu³⁺ centers only coordinate with O-sites from carboxylate groups. Therefore, the energy transfer between ligands and Cu centers will be more effective than the one between ligand and Eu³⁺ centers.





Fig. S6 FT-IR spectra of **NBU-8** (a) as well as its solid samples (b and c) after being immersed in various solvents for 24 h.



Fig. S7 The luminescence spectra of **NBU-8** after incubated for 24 h under various solvents when excited at 237 nm.



(A) NBU-8 in CH_3CN for 2 weeks (B) NBU-8 in DMF for 2 weeks

Fig. S8 The image of **NBU-8** (15 mg) after being immersed in CH₃CN and DMF solvents (2 mL), respectively, for 2 weeks.



Fig. S9 The XRD powder patterns for freshly synthesized compound **NBU-8** and after being immersed in DMF solvent for two weeks.





Fig. S10 (a) Liquid UV-vis spectra of various organic solvents as well as the solid UV-vis spectra (absorbance) of **NBU-8** in solid state (b) at room temperature.



Fig. S11 The luminescence spectra of **NBU-8** with different particle sizes after being immersed in DMF solution at various time intervals at room temperature ($\lambda_{ex} = 237$ nm).

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