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A hetero-MOF-based bifunctional ratiometric fluorescence sensor for pH and water detection

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The detections of pH and water are of significance in natural and production processes. The ionothermal reactions of 4,4'oxybisbenzoic acid (H₂OBA) with Eu³⁺ and/or Tb³⁺ produced [M(OBA)(H₂O)CI] (M = Eu³⁺ (1) and Tb³⁺ (2)), and heteronuclear [Eu_{0.05}Tb_{0.95}(OBA)(H₂O)CI] (**3**). **3** emits the combined characteristic transitions of Eu³⁺ and Tb³⁺. Its energy transition processes can be disturbed by pH and water. The emission colors of **3** follow pH changes. It emits blue light when pH = 1-2, in which OBA²⁻ turns to H₂OBA based on the acid-base equilibrium. As pH = 3-11, the emission colors transfer from green to orange and I_{Tb}/I_{Eu} exhibits a linearity of I_{Tb}/I_{Eu} = 6.7482–0.5971·pH; the emissions are quenched at pH = 12-13, due to OH⁻ destroying the delocalized conjugated system of **3**. **3** shows a fluorescence response to water with a linearity of I_{Tb}/I_{Eu} = 0.30353 + 0.15042·V_{H2O}% within 0-0.8% V_{H2O}%. The green (G) and red (R) color intensities of paper-based MOF sensor of **3** reveal a trinomial fitting equation of G/R = 4.16334–1.23014·pH+0.14036·pH²–0.00551·pH³ when pH = 3-11. **3** as a ratiometric fluorescence sensor can be used to detect pH and water and the paper-based MOF sensor also can be used in on-site pH detection.

Introduction

pH value is one of the most important physical and chemical parameters of an aqueous solution. A lot of natural phenomena, chemical changes and production processes involving aqueous solutions concern with pH value.^{1,2} The seemingly simple pH measurement can affect the whole process. Abnormal pH in human body, such as intracellular acidification (pH 4.5–6.0), is often relevant to many pathological processes, like inflammation, tumorgenesis, and cystic fibrosis.^{3,4} Therefore, it is highly valuable to precisely monitor pH value in many fields like industry, agriculture, medicine, environmental protection and scientific research. ^{5,6} For a laboratory analysis, pH measurement is often the most basic experimental means. Generally, there are three ways to measure pH in laboratories: pH indicator, pH test paper and pH meter. However, the accurate pH value cannot be indicated by pH indicator though it can determine the pH range; the pH test paper cannot accurately show

the pH value, also not one of an oily solution; a pH meter can determine pH to two decimal places, but many limits like aqueous solution, temperature, and equipment maintenance block its application in more complicated environments.⁷⁻⁹

Recently, optical methods have received much attention due to the high sensitivity, fast response, easy miniaturization, noninvasion and high throughput.¹⁰ Especially, fluorescence pH sensors have been widely applied,¹¹ which utilize the emission changes to detect pH. However, their determination accuracy is frequently compromised by external environment, such as fluctuations in the source intensity, photo bleaching of the sensor, and analyte concentration, leading to an unreliable result.¹²⁻¹³ In contrast, the ratiometric fluorescence pH sensors employ the ratio of two emissions at different wavelengths as the detecting signal, providing a built-in correction for the external factors and allowing for a more accurate determination.¹⁴ Dual central lanthanide metal-organic frameworks (Ln-MOFs) integrate two luminescent centers and chromophoric sensitizers in a single molecular system, exhibiting a color tunability and a self-calibration without sensitivity to outside.¹⁵ The dual central Ln-MOFs have a promising prospect in ratiometric fluorescent pH sensors.

4,4'-oxybisbenzoic acid (H₂OBA) comprises of several functional oxygen atoms in the central ether and terminal carboxylate groups. These oxygen atoms can form supramolecular interactions, such as hydrogen bonds and electrostatic interactions. Thereby their existence forms can be influenced by H⁺, OH⁻ and H₂O, thus to change the energy level of (H)OBA ligand and pass the influence to

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⁺⁺Electronic Supplementary Information (ESI) available: Experiments, EDS, structural determination and refinement, PXRD, TG, Fluorescence, IR, Fluorescence lifetime, durability, low-temperature phosphorescence spectrum, and UV. CCDC 2027427 (1). See DOI: 10.1039/x0xx00000x.

its fluorescent property.¹⁶⁻¹⁸ The revealed relationship between external conditions and fluorescence will realize the recognition of a specialized molecule. Therefore, (H)OBA-containing heteronuclear Ln-MOF with the hydrophilic ether and carboxylate moieties are very suitable for monitoring pH value or water that can easily form supramolecular bonds. It will provide new opportunities for (H)OBA-containing Ln-MOFs to detect pH and water.

Herein, we selected H₂OBA as the ligand and Eu³⁺/Tb³⁺ as metal sources to synthesize single metal compounds [M(OBA)(H₂O)Cl] (M = Eu³⁺ (1), Tb³⁺ (2)) and heteronuclear [Eu_{0.05}/Tb_{0.95}(OBA)(H₂O)Cl] (3)). The single crystal structure of 1 was resolved, and 1-3 were determined to have the same structures by powder X-ray diffraction (PXRD). **3** was used as a fluorescence sensor to detect pH and water content. The sensitivity tests of **3** to pH and water were carried out and showed linear equations of I_{Tb}/I_{Eu} =6.7482-0.5971·pH in the pH range of 3-11 and I_{Tb}/I_{Eu} = 0.30353 + 0.15042·V_{H2O}% within 0-0.8% V_{H2O}% respectively, indicating **3** is a bifunctional ratiometric fluorescence sensor to pH and trace water. Its paper-based MOF sensor displayed obvious emission color conversions at pH = 3, and a trinomial equation of G/R = 4.16334–1.23014·pH+0.14036·pH²–0.00551·pH³, showing a prospect in a rough on-site pH detection.

Results and discussion

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Synthesis and Basic characterizations

1-3 were synthesized in ionothermal reactions. Ionothermal synthesis using ionic liquids as reaction media distinguishes itself with features of high ionic conductivity, non-flammability, negligible vapor pressure. Different from traditional hydro(solvo)thermal synthesis, ionothermal synthesis contributes to new types of materials with intriguing structures based on the high polarity environment. 1-3 are allomeric, whose experimental PXRD patterns are as same as the simulated one from the single crystal data (ESI, Fig. S1). Also, the identity of 1 and the simulated pattern indicates that the bulk sample of 1 was isolated with high phase purity. Energydispersive X-ray spectroscopy (EDS) was used to confirmed Tb³⁺ and Eu³⁺ contents in the heteronuclear **3** (ESI, Table S1). The average elemental content ratio of Eu³⁺:Tb³⁺ is 0.47:8.72. The Eu³⁺:Tb³⁺ ratios (1:18.55) is close to the starting feeding 1:19. Therefore, the formula of **3** can be determined as $[Eu_{0.05}Tb_{0.95}(OBA)(H_2O)CI]$. The thermal stabilities of 1-3 were evaluated by thermogravimetric analysis (TGA). Totally, 2 and 3 show very similar thermal decomposition behaviours and a slightly difference from 1. The TG curves indicate that 1-3 remain stable around 200 °C, 214 °C for 1, 192 °C for 2, and 194 °C for 3 (ESI, Fig. S2). There are small weight losses of 3.50% for 1 before 281 °C, 4.63 % for 2 before 239 °C and 3.99 % for 3 before 239 °C, which can be assigned to the loss of the coordinated water. The water losses are close to the theoretical values: 3.90 % for 1, 3.84% for 2 and 3. There are major weight losses follows: 44.71% in 281-549 °C, 29.56% in 239-630 °C, and 29.53% in 239-634 °C. These major weight losses are attributed to the loss of a part of OBA²⁻ ligand (the weight loss is much less than the calculated ones).

Crystal structures of 1-3

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For clarity, only 1 is discussed its crystal structure in detail. 1 crystallizes in a monoclinic P21/c space group, whose structural determination and refinement data were listed in ESI, Table S2. Its asymmetry structural unit comprises of one Eu(III), one Cl-, one OBA²⁻, and one H₂O. Eu(III) locates in a seven-coordinated single-cap triangular prism containing one H₂O, four oxygen atoms from two OBA²⁻ ligands and two Cl⁻. Two neighboring Eu³⁺ centers are connected by two pairs of -COO⁻ groups in two μ_4 - $\eta^2\eta^2$ -OBA²⁻ ligands into a [Eu₂(COO)₂(H₂O)₂] second building unit (SBU) (Fig. 1). Two Eu(III) in neighboring $[Eu_2(COO)_2(H_2O)_2]$ SBUs are connected by one group of a Cl⁻ anion and a O11-C17-O12 bridge into a six-membered $[Eu_2Cl(COO)]$ ring. The connection of four $[Eu_2Cl(COO)]$ rings alternatively with four [Eu2(COO)2(H2O)2] SBUs shapes a 24membered ring, whose growth forms a lattice-like a 2D layer in bcplane. The point symbol of the simplified 2D layer is 2,8-connected 2-nodal {4⁴.8¹⁶.12⁸}{4}₄ (ESI, Fig. S3). The 2D layers are further connected into a 3D architecture by the residual part of OBA2ligands. The 3D architecture was calculated and simplified by dummying [Eu₂(COO)₂(H₂O)₂] SBU, Cl⁻, and the residual part of OBA²⁻ as 8, 2, and 2-connecting nodes, respectively. The point symbols are {8} for Cl⁻, {4} for the residual part of OBA²⁻, and $\{4^2.8^{20}.12^6\}$ for [Eu₂(COO)₂(H₂O)₂] SBU. Therefore, the overall topological structure of **1** can be simplified as a 2,2,8-connected 3-nodal {4².8²⁰.12⁶}{4}₂{8}₂ (ESI, Fig. S4).



Fig. 1. The structural construction of 1.

Solid-state fluorescence. The solid-state emission spectra of **1-3** were recorded at ambient temperature under excitation at *ca*. 280 nm (ESI, Fig. S5). **1** exhibited a red fluorescence with emissions at *ca*. 595(middle), 616(strong), 656(weak) and 703 nm (weak), originating from the ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 1-4) transitions of Eu³⁺ center (Fig. 2). **2** emitted green fluorescence with emissions at 490 (middle), 545 (strong), 587 (weak) and 620 nm (weak), coming from the characteristic ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (J = 6-3) transitions of Tb³⁺ center.¹⁹ **3** displayed reddish orange emissions at 490 (weak), 547 (weak), 594 (weak), 616 (strong), 701 nm (weak), which are the combined characteristic emissions of Tb³⁺ and Eu³⁺. The emission colors of **1-3** are accord with the CIE 1931 chromaticity diagram (Inset of Fig. 2). **1-3** also presented small

emission quantum efficiencies: 2.2% at 616 nm for **1**, 81.8% at 547 nm for **2**, and 8.9% at 616 nm for **3**.



pH detection

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3 were dispersed in HCl or NaOH solutions with pH = 1-13, whose liquid emission spectra were recorded at ambient temperature (Fig. 3). 3 remained structural stability when immersed in the aqueous solutions for 2h with pH = 1-13 (ESI, Fig. S6). Comparing the emission spectra, besides the characteristic emissions of Tb³⁺ and Eu³⁺, there are strong blue emissions centered at 325 nm as pH = 1-2 which are assigned to the intraligand $\pi \cdots \pi$ transition. With pH increasing from 3 to 11, the emissions of the ligand were weakened. The relative emission intensities of Tb³⁺ (the emission of ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ at 547 nm) and Eu³⁺ (the emission of ⁵D₀ \rightarrow ⁷F₂ at 616 nm) (I_{Tb}/I_{Eu}) gradually decreases depending on the increased pH in range of 3-11 and the emission colors gradually change from greenish (pH = 3-7) to reddish (pH = 8-7) 11). At pH = 12-13, owing to OH⁻ destroying the delocalized conjugated system of 3, the emissions are quenched (Inset of Fig. 3) along with the emission from ligand disappeared. It indicates higher pH is helpful for OBA²⁻ ligand to stay at a lower energy level to sensitize Eu³⁺ more effectively. The plot of I_{Tb}/I_{Eu} vs pH shows a good linearity between $I_{\text{Tb}}/I_{\text{Eu}}$ and pH in the range of 3-11. The linear equation is $I_{Tb}/I_{Eu} = 6.7482 - 0.5971 \cdot pH$ with a correlation coefficient R^2 = 0.98316. The situation of I_{Tb}/I_{Eu} decreasing with pH is related with the formation of weak contacts between OBA²⁻ ligands and H⁺/OH⁻. In the strong acidic environment, H⁺ cations tend to combine with the electron-rich groups, such as COO⁻ groups to make the acidbase equilibrium of OBA²⁻ ligands back to partly protoned (H)OBA ligands. It leads to similar intraligand $\pi \cdots \pi$ transition as free H₂OBA (λ_{em} = 326 nm). As weak contacts formed and electron transferred, the reduced electronic density in OBA²⁻ ligands led to an increased triplet energy level. Therefore, OBA2- ligands prefer to excite Tb3+ with larger energy difference, making the emission color greenish in low pH. As pH increasing, especially in alkaline environment, OHbinds to OBA²⁻ ligands, destroying the delocalized conjugated system of 3. OBA²⁻ ligands turn to excite Eu³⁺ with smaller energy difference, resulting in an emission color transfer from green to red. Comparing to the reported pH sensors, we can find the linear range of 3



detecting pH is wide and covers acidic and alkaline environments at



Fig. 3. (a) Emission spectra of **3** dispersed in HCl or NaOH solutions with pH ranging 1-13 (Inset: the linear relationship of I_{Tb}/I_{Eu} vs pH and the photos of the emission colors in pH range of 3-11).

Table 1. The pH detection performances of 3 and the reported sensors

Sensor	Methods	Linear ranges	Refs
Eu _{0.05} Tb _{0.95} (OBA)(H ₂ O)Cl	fluorometric	3-11	This work
[H ₃ O][Eu ₃ (HBPTC) ₂ (BPTC))(H ₂ O) ₂]·4DMA	Fluorometric	7.5 - 10.0	11
MPDB-PCN	Colorimetric,	2.51-5.78,	14
Eu _x Tb _{1-x} Hdpda	Colorimetric, fluorometric	3.9-7.5	15
Cd-EDDA	Fluorometric	2.0-6.5 <i>,</i> 9.5-11.5	16
Zn-cpon-1	Fluorometric	2.0-6.5, 8.0-11.5	17
({(Me ₂ H ₂ N)[Eu(L)]·DMF· H ₂ O}n)	Fluorometric	3-7	20
Eu _{0.034} Tb _{0.966} -NMOF	Colorimetric, fluorometric	3-7	21
DMF–Tb–Phen	Fluorometric	1.03-3.5	22
NU-1000-CNF	Fluorometric	2-9	23
[Eu ₂ (NDC) ₃ (DMF) ₂]·DMF	Fluorometric	3-4	24
Al-MIL-101-NH ₂	Fluorometric	4.0-7.7	25
CDs@UiO-66(OH)2	Fluorometric	3-7	26
Eu ₃₊ @UiO-67-bpydc	Fluorometric	1.06-10.99	27
COF-HQ	Fluorometric	1-5	28
Zr ₆ (µ ₃ -O) ₄ (µ ₃ -OH) ₄ (ITTC) ₄	Fluorometric	0-1.04, 10.2-11.08	29
Fe ₃ O ₄ NPs@PCN-224	Fluorometric	1-7	30
[Eu(PPTA) _{0.5} (NO ₃)(DMF) ₂]·H ₂ O	Fluorometric	2-7,7-10.5	31
N-doped carbon dots	Fluorometric	2-8,7-14	32
MOF1-P BDR	Fluorometric	3-8	33

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 Ευ/Th-ΡΜΔ	Colorimetric,	2-5 5	34
20,10100	fluorometric	2 3.3	
(4-MPy)-linked (BMP)	Fluorometric	20	25
SERS-based pH sensor		3-8	35
{[Tb(TATAB)	Fluorometric	7 5 10 0	26
(H ₂ O) ₂]·NMP·H ₂ O}n		7.5-10.0	30
Eu3t@Mn tabac	Colorimetric,	1 4 12 14	37
	Fluorometric	1-4,12-14	

Water detection

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3 was separately dispersed in eleven kinds of pure solvents: tetrahydrofuran (THF), carbon tetrachloride (CCl₄), cyclohexane, dimethylformamide (DMF), 1,4-dioxane, chloroform, N,N-dimethylacetamide (DMAC), isopropanol, ethanol, methanol and water. Fig. 4 indicates that **3** emits similar fluorescence and I_{Tb}/I_{Eu} remains similar intensities in all solvents except water (see inset in Fig. 4a). It is clear that **3** emits bright green light in water, which inspires us the possibility for **3** to cause fluorescence response to water.

The effect of trace water on the fluorescence of 3 was investigated by preparing DMF/H₂O mixed solutions with volume fraction of H₂O (V_{H20}%) ranging 0-40% (Fig. 4b). The emission intensities at 547 nm from Tb³⁺ are increased and those at 616 nm remain stable with V_{H20}%. The photos taken under UV lamp at 254 nm (inset of Fig. 4b) are accorded with the CIE 1931 chromaticity diagram (ESI, Fig. s7a), showing the emission colors change from red via orange to green. As $V_{\rm H2O}\%$ fixed at 0-0.8%, the similar phenomena occurred as the situation in V_{H2O} % of 0-40% (ESI, Fig. S7b). I_{Tb}/I_{Eu} gradually increase depending on V_{H2O} %, in which a linear relationship of $I_{Tb}/I_{Eu} = 0.30353$ + 0.15042·V_{H20}% (R^2 = 0.9958) between I_{Tb}/I_{Eu} and V_{H20}% (inset of Fig. 4b). It is can be interpreted by the formation of hydrogen bonds between solvent water and the coordination water in 3. Hydrogen bonds result in an increased emission intensity at 547 nm and increased I_{Tb}/I_{Eu} .³⁸⁻³⁹ The fluorescence lifetimes (FLTs) of the emission from Tb³⁺ at 547 nm and the one from Eu³⁺ at 616 nm were recorded at ambient temperature. FLTs of Eu^{3+} in the samples with $V_{H2O}\% = 0\%$, 10%, 20%, 30% and 40% are 560.87, 481.33, 489.53, 496.55 and 502.48 µs respectively (ESI, Fig. S8a), locating in a very narrow range and showing a slightly increased trend with V_{H20} %. While, FLTs of Tb³⁺ are 47.52, 99.28, 289.64, 393.70 and 472.21 µs respectively for the samples with V_{H2O} % = 0-40% (ESI, Fig. S8b). A clear trend can be seen that FLTs of Tb³⁺ greatly increased with V_{H20}%. The trend in FLTs changes agrees with the changes in the emission intensity, supporting the energy distribution between Eu³⁺ and Tb³⁺. As comparing to the reported water sensors in Table 2, it is clear that LOD of **3** is larger than most of the sensors and the linear range is more limited. With an extension test, 3 was used to measure the water content in DMAC solution, which showed similar detection performance with a linearity of $I_{Tb}/I_{Eu} = 0.2942+0.21553 \cdot V_{H2O}\%$ (R² = 0.98124) (ESI, Fig. S9).



Fig. 4. (a) The emission spectra of **3** dispersed in THF, CCl₄, cyclohexane, DMF, 1,4-dioxane, chloroform, DMAC, isopropanol, ethanol, methanol, and water (inset: the plot of I_{Tb}/I_{Eu} in different solvents and the photos taken under UV lamp at 254 nm); (b) the emission spectra of **3** with V_{H2O}% ranging at 0-40% (inset: the linear fitting plot between I_{Tb}/I_{Eu} vs V_{H2O}% ranging 0-0.8% and the photos taken under UV lamp at 254 nm).

Table 2. The water detection performances of 3 and the reported sensors.

Sensor	Methods	LOD (%, v/v)	Linear range (%, v/v)	refs
Eu _{0.05} Tb _{0.95} (OB A)(H ₂ O)Cl	Colorimetric, fluorometric	0.10	0-0.8	This work
PCM-22	Colorimetric, fluorometric	0.1	10- 120000 ppm	39
Eu-DPA/PTA- NH ₂	Colorimetric, fluorometric	0.01	0-100	40
Tb _{97.11} Eu _{2.89} - L ₁	Colorimetric, fluorometric	0.04	0-2.5	41
AEMOF- 1·DMAc	Fluorometric	-	0.05-5	42
Eu-MOFs/N,S- CDs	Colorimetric, fluorometric	0.03	0.05-30	43
Eu _{0.02} Dy _{0.18} - MOF	Colorimetric, fluorometric	-	0-10	44
[Ln₂Cl ₆ (bipy)₃]· 2bipy	Fluorometric	-	0.1-10	45
Zn(hpi2cf)(DM F)(H ₂ O)	Fluorometric	-	0.05-1.3	46

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Ru@MIL-NH ₂	Colorimetric, fluorometric	0.02	0-100	47
(Eu(atpt) _{1.5} (H ₂ O)n)	Colorimetric, fluorometric	0.02	0.05-6	48

Durability Test

The durability of **3** detecting pH was tested by repeating five cycles. **3** was immersed in aqueous solution with pH = 3, 7 and 11, whose liquid fluorescence were characterized, then was washed and dried at 120 °C for 1h. This process was repeated for five times. The PXRD patterns of **3** in five cycles was as same as that **3** before cycles, demonstrating that **3** remained the structural stability in the detection cycles (ESI, Fig. S10). The relative emission intensities I_{Tb}/I_{Eu} stayed basically stable at pH = 3, 7 and 11 during five cycles, though with some fluctuations (ESI, Fig. S11). Also, **3** remained enough sensitivity to pH with emission color changed. It indicates that **3** has enough durability to carry out the pH detection.

Paper-based MOF detection of pH

3 was dispersed in absolute ethanol and deposited on the test paper to prepare paper-based MOF sensor. The paper-based MOF sensor was used to detect pH with photos taken under UV lamp at 254 nm (Fig. 5). The aqueous solutions with pH = 3, 5, 7, 9, 11 and 13 were also checked by the paper sensor. The emission color of the one with pH = 13 was quenched. In pH range of 3-11, the emission colors changed from green via orange to red (Inset of Fig. 5), whose green (G) and red (R) color intensities were recognized. The plot of G/R ratio *vs* pH was depicted (Fig. 5). A trinomial fitting equation of G/R = 4.16334–1.23014·pH+0.14036·pH²–0.00551·pH³ (a correlation coefficient R^2 = 0.99972) when pH = 3-11. It suggests the possibility that paper-based sensor of **3** can be used in the rough on-site detection of pH by naked eyes. In summary, this work presented a facile, portable and cost-effective paper-based visual sensor for rapid monitoring pH by using test paper immobilized with **3**.



Fig. 5. A plot of G/R ratio vs pH of the paper-based sensors immobilized **3** detecting pH ranging 3-11 (inset: the photo of emission colors taken under UV lamp at 254 nm with the inside numbers representing pH).

Fluorescence and detection mechanism

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The PXRD pattern of [Gd(OBA)(H₂O)Cl] is as same as 1-3 (ESI, Fig. S12a). Therefore, allomeric $[Gd(OBA)(H_2O)CI]$ can be used to calculate the triplet energy level (T1) of OBA²⁻ ligand by eliminating the structural effect. The low-temperature phosphorescence spectrum of [Gd(OBA)(H₂O)Cl] at 77 K was measured and showed emissions starting at 391 nm under the excitation at 270 nm (ESI, Fig. S12b). T1 of OBA²⁻ ligand in this work is calculated as 25575 cm⁻¹. The emitting levels of the intenest ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ of Eu³⁺ and ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ of Tb³⁺ are 17200 and 20500 cm⁻¹. The energy differences between T1 of OBA²⁻ and Ln^{3+} are 8375 (for Eu^{3+}) and 5075 cm⁻¹ (for Tb^{3+}). According to Latva's rules, an optimal ligand-to-metal energy transfer process for a Ln^{3+} needs $\Delta E = [E(T1) - E(^{5}D_{J})]$: 2500-4500 cm⁻¹ for Tb³⁺ (⁵D₄) and 2500-4000 cm⁻¹ for Eu³⁺ (⁵D₀).⁴⁹ Relatively, ΔE between OBA²⁻ and Tb³⁺ indicated that T1 of OBA²⁻ basically matched the energy levels of Tb^{3+} (${}^{5}D_{4}$), but not for Eu^{3+} (${}^{5}D_{0}$). Therefore, OBA²-ligand could transfer the excited energy to Tb³⁺ efficiently but not populate Eu³⁺ efficiently. However, the emission color of 3 is reddish orange, not green, even though the molar ratio of Tb³⁺ to Eu³⁺ is 19:1. This means the red emission of Eu³⁺ is dominant. The intermetallic energy transfer from Tb³⁺ to Eu³⁺ can account for the orange emission. The energy transformation efficiency $(\tau_0 - \tau)/\tau_0$ (τ : FLT; $\tau_0 = 424.9 \ \mu s$; $\tau = 84.98 \ \mu s$) of Tb³⁺ to Eu³⁺ is up to 80% (ESI, Fig. S12).

pH plays an important role in the fluorescence of 3. In pH detection, OBA^{2-} ligand link with H⁺ as pH = 1-3, resulting in protonation in OBA2- based on the acid-base equilibrium of OBA2-. It can be clearly seen in FT-IR spectra that 3 immersed in HCl solution with pH = 1-3 exhibited the same vibration frequency of -COOH group (ESI, Fig. S13), confirming OBA²⁻ turns to H₂OBA in acid-base equilibrium. This protonation leads to the recurrence of the disappeared emission at 326 nm from the ligand. While, 3 immersed in NaOH solution of pH = 10-12 exhibited the same vibration frequency of 3 with deprotoned -COO- groups. No emission from ligand can be found. In the situation of strong basic medium (pH =13), the emissions are guenched. FLTs of Tb³⁺ and Eu³⁺ in 1-3 are depicted (ESI, Fig. S14). FLTs of Tb³⁺ in **3** (84.98 µs) become greatly shorter than the one in 2 (424.9 μs) and those of Eu³⁺ become a little longer (337.8 μ s in **1** and 461.63 μ s in **3**). It is related with the intermetallic energy transfer from Tb³⁺ to Eu³⁺, shortening FLTs of Tb³⁺ and lengthening FLTs of Eu³⁺. With increased pH, FLTs of Eu³⁺ in 1 are much shorter than those in **3**. While FLTs of Tb³⁺ in **2** are longer than those in **3**. FLTs of Tb³⁺ in **3** are longer in acid than in base. It agrees that the interrupted energy transfer from Tb³⁺ to Eu³⁺ help to prolong FLTs of Tb³⁺. Under alkaline environment, the energy transfer from Tb³⁺ to Eu³⁺ recovered, thus the emission colors also reverted from orange to red (ESI, Fig. S15).

As H₂O added, solvent water forms hydrogen bonds with the coordination of H₂O, making the intermetallic energy transfer from Tb³⁺ to Eu³⁺ interrupt.⁴¹ The emission color of **3** was changed from reddish to green. With the V_{H2O}% increased, the emission of Tb³⁺ occupied main proportion. FLTs of Tb³⁺ increased with V_{H2O}% and

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those of Eu^{3+} stayed stable (ESI, Fig. S8), demonstrating the formation of hydrogen bonds with H₂O benefits the emission of Tb³⁺ and interrupts the intermetallic energy transfer from Tb³⁺ to Eu³⁺.

Conclusion

H₂OBA reacted with Eu³⁺ and/or Tb³⁺ to produce single lanthanide MOFs 1 and 2, and heteronuclear 3. 1-3 are allomeric compounds, whose PXRD patterns are as same as the simulated one of 1 from single crystal data. The fluorescence properties of 1-3 are relevant to the characteristic transitions of Ln^{3+} (${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 1-4) for Eu³⁺ in 1 or ${}^{5}D_{4} \rightarrow {}^{7}F_{1}$ (J = 6-3) for Tb³⁺ in **2**). **3** emitted the combined characteristic transitions of Eu³⁺ and Tb³⁺. The fluorescence mechanism was interpreted by LMCT from OBA²⁻ to Eu³⁺ and Tb³⁺ with the synergistic intermetallic energy transfer from Tb³⁺ to Eu³⁺. The matched energy difference between OBA^{2-} and Tb^{3+} indicates the higher energy transformation efficiency from OBA2- to Tb3+. The intermetallic energy transfer efficiency from Tb³⁺ to Eu³⁺ up to 80% clearly explains the emission color being reddish not green. 3 is a bifunctional ratiometric fluorescence sensor for pH and water. It emits blue light at 326 nm assigned to intraligand $\pi \cdots \pi$ transition when pH = 1-2, which concerns with the acid-base equilibrium of OBA²⁻ transferring to (H)OBA. The relative emission intensities at 547 nm (Tb³⁺) and 616 nm (Eu³⁺) (I_{Tb}/I_{Eu}) exhibit a good linearity of I_{Tb}/I_{Eu} = 6.7482–0.5971·pH with a correlation coefficient $R^2 = 0.98316$ in the pH range of 3-11. 3 shows fluorescence response to water: the emission intensity increases with water content. I_{Tb}/I_{Eu} displays a linear relationship of $I_{Tb}/I_{Eu} = 0.30353 + 0.15042 \cdot V_{H20}\%$ ($R^2 = 0.9958$) when $V_{\rm H2O}\%$ within 0-0.8%. FLTs of Tb^{3+} greatly increase with $V_{\rm H2O}\%$ and those of Eu³⁺ stay stable, supporting the analysis of energy distribution between Eu³⁺ and Tb³⁺. The paper-based MOF sensor of 3 was used to on-site detect pH. The green (G) and red (R) color intensities were recognized and the plot of G/R ratio vs pH was depicted. It reveals a trinomial fitting equation of G/R = $4.16334 - 1.23014 \cdot pH + 0.14036 \cdot pH^2 - 0.00551 \cdot pH^3$ ($R^2 = 0.99972$) when pH = 3-11. Our work suggests that 3 as a bifunctional ratiometric fluorescence sensor can be used to detect pH and water. Its paper-based MOF sensor also can be used in the rough on-site detection of pH by naked eyes. In summary, this work presented a facile, portable and cost-effective paper-based visual sensor for rapid monitoring pH by using test paper immobilized with 3.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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View Article Online DOI: 10.1039/DODT03626A A hetero-MOF-based bifunctional ratiometric fluorescence sensor for pH and

water detection

Hong Li, Bing Liu, Ling Xu* and Huan Jiao*



Ratiometric fluorescence sensor $[Eu_{0.05}Tb_{0.95}(OBA)(H_2O)Cl]$ detect pH and water, whose paper-based sensor can be applied in on-site pH detection.