WILEY-VCH

Supporting Information

Colorimetric Sensor Array for Amines based on Responsive Lanthanide Complex Entrapment

*Peng Li, Zhiqiang Li, Decui Yao, and Huanrong Li**

School of Chemical Engineering and Technology, Hebei University of Technology,

Guang Rong Dao 8, Hongqiao District, Tianjin 300130, P. R. China.

*E-mail: lihuanrong@hebut.edu.cn

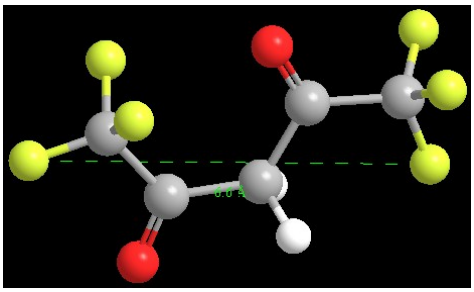


Figure S1 Molecular structure of HFA.

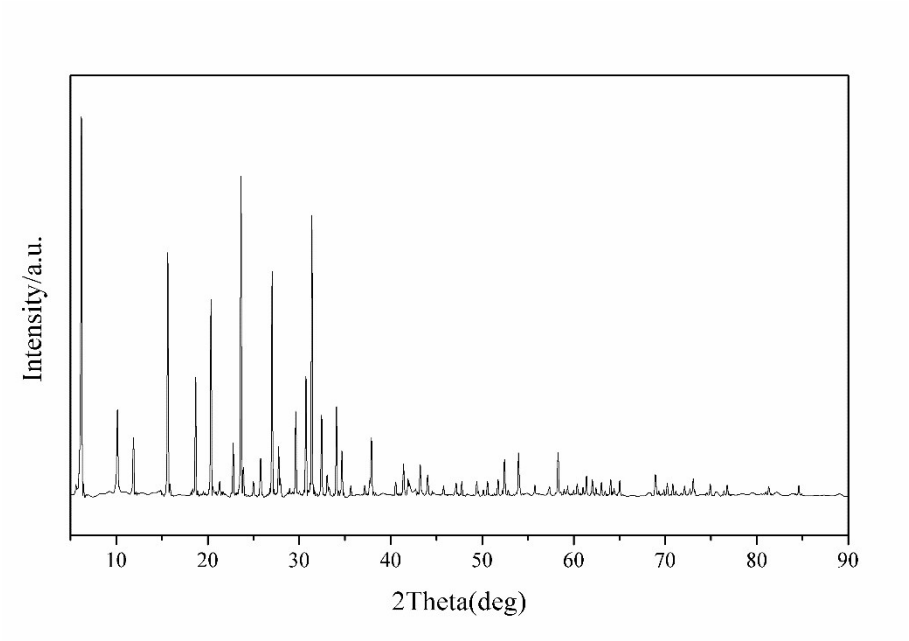


Figure S2 XRD pattern of zeolite Y (ZY)

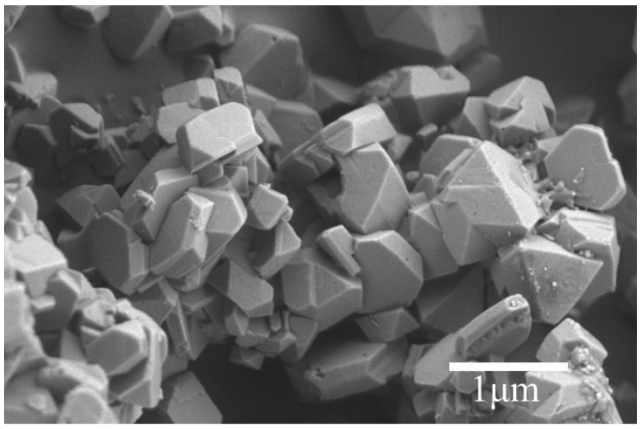


Figure S3 SEM images of zeolite Y (ZY)

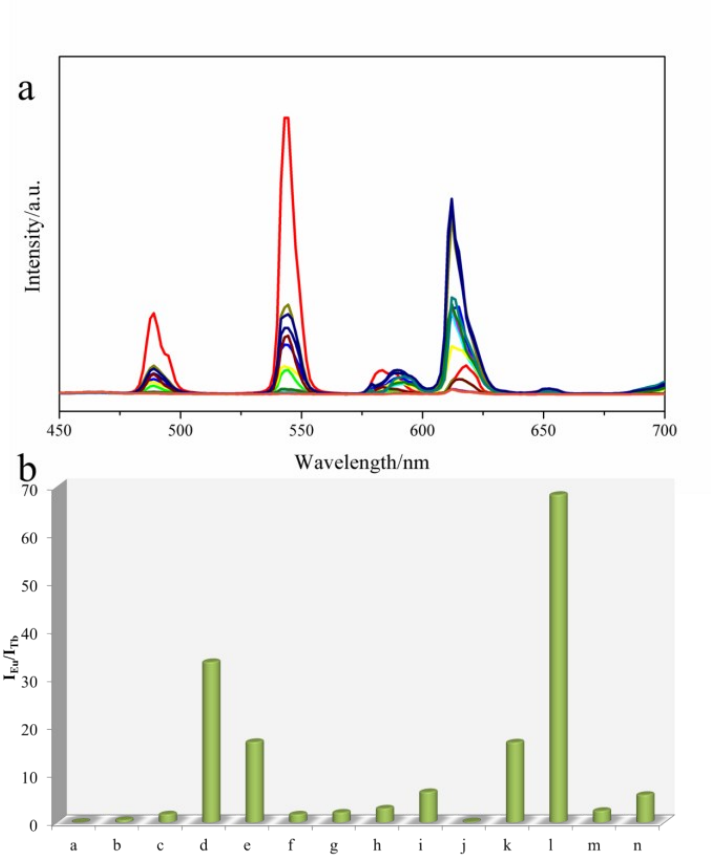


Figure S4 a) Emission spectra of $Eu_1Tb_9(HFA)_n$@ZY after treatment with various amine vapors using an excitation wavelength of 302 nm. ($Eu_1Tb_9(HFA)_n$@ZY (red line), aniline (green line), Benzylamine (blue line), Propylamine (cyan line), 1,3-Propanediamine (magenta line), Ethylenediamine (yellow line), Triethylamine (dark yellow line), Cyclohexylamine (navy line), Methylamine (purple line), N- Methylaniline (wine line), Butylamine (olive line), ammonia (dark cyan line), Tert-butylamine (royal line), Ethylamine (orange line)) b) The relative emission intensity at 612 nm and at 544 nm (I_{Eu}/I_{Tb}) of $Eu_1Tb_9(HFA)_n$@ZY excitated at 302 nm upon treatment with various amine solvent vapors. (a: $Eu_1Tb_9(HFA)_n$@ZY, b: Aniline, c: Benzylamine, d: Propylamine, e: 1,3-Propanediamine, f: Ethylenediamine, g: Triethylamine, h: Cyclohexylamine, i: Methylamine, j: N- Methylaniline , k: Butylamine, l: Ammonia, m: Tert-butylamine and n: Ethylamine)

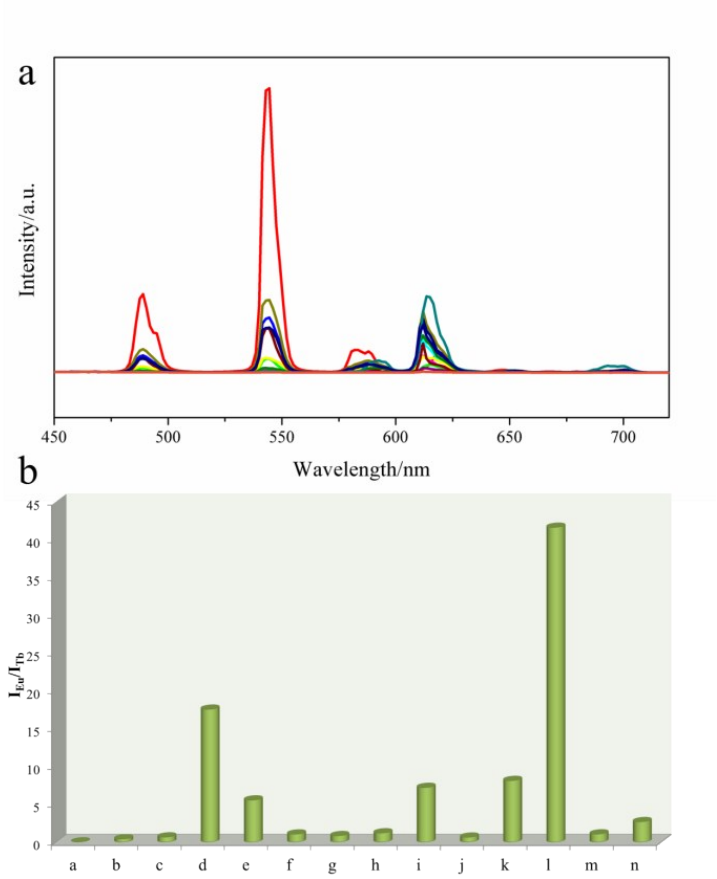


Figure S5 a) Emission spectra of $Eu_{0.5}Tb_{9.5}(HFA)_n$@ZY after treatment with various amine vapors using an excitation wavelength of 302 nm. ($Eu_{0.5}Tb_{9.5}(HFA)_n$@ZY (red line), aniline (green line), Benzylamine (blue line), Propylamine (cyan line), 1,3-Propanediamine (magenta line), Ethylenediamine (yellow line), Triethylamine (dark yellow line), Cyclohexylamine (navy line), Methylamine (purple line), N- Methylaniline (wine line), Butylamine (olive line), ammonia (dark cyan line), Tert-butylamine (royal line), Ethylamine (orange line)) b) The relative emission intensity at 612 nm and at 544 nm (I_{Eu}/I_{Tb}) of $Eu_{0.5}Tb_{9.5}(HFA)_n$@ZY excitated at 302 nm upon treatment with various amine solvent vapors. (a: $Eu_{0.5}Tb_{9.5}(HFA)_n$@ZY, b: Aniline, c: Benzylamine, d: Propylamine, e: 1,3-Propanediamine, f: Ethylenediamine, g: Triethylamine, h: Cyclohexylamine, i: Methylamine, j: N- Methylaniline , k: Butylamine, l: Ammonia, m: Tert-butylamine and n: Ethylamine)

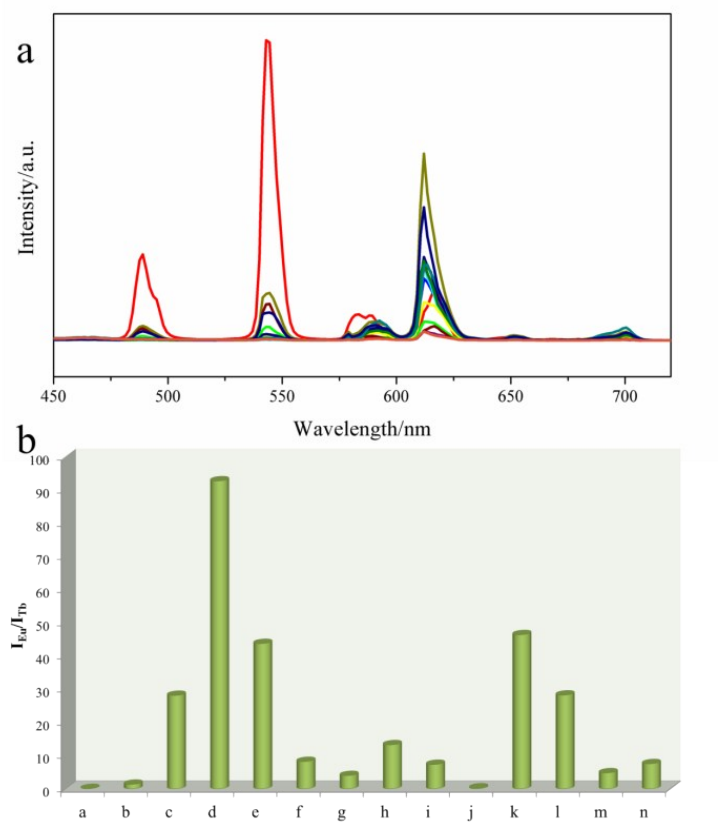


Figure S6 a) Emission spectra of $Eu_2Tb_8(HFA)_n$@ZY after treatment with various amine vapors using an excitation wavelength of 302 nm. ($Eu_2Tb_8(HFA)_n$@ZY (red line), aniline (green line), Benzylamine (blue line), Propylamine (cyan line), 1,3-Propanediamine (magenta line), Ethylenediamine (yellow line), Triethylamine (dark yellow line), Cyclohexylamine (navy line), Methylamine (purple line), N- Methylaniline (wine line), Butylamine (olive line), ammonia (dark cyan line), Tert-butylamine (royal line), Ethylamine (orange line)) b) The relative emission intensity at 612 nm and at 544 nm (I_{Eu}/I_{Tb}) of $Eu_2Tb_8(HFA)_n$@ZY excited at 302 nm upon treatment with various amine solvent vapors. (a: $Eu_2Tb_8(HFA)_n$@ZY, b: Aniline, c: Benzylamine, d: Propylamine, e: 1,3-Propanediamine, f: Ethylenediamine, g: Triethylamine, h: Cyclohexylamine, i: Methylamine, j: N- Methylaniline , k: Butylamine, l: Ammonia, m: Tert-butylamine and n: Ethylamine)

Table S1 The emission lifetimes of $Tb(HFA)_n$@ZY before (τ_{Tb}) and after treatment with various amine vapors (τ_{Tb}') and the energy back-transfer rates lnk_{back} from the emitting level of the Tb^{3+} ion to the excited triplet state of HFA.

	$Tb(HFA)_n$@ZY	Triethylamine	Benzylamine	Aniline	Butylamine
τ_{Tb} (τ_{Tb}') /ms	0.351	0.302	0.146	0.183	0.163
lnk_{back}/s^{-1}		6.136	8.294	7.872	8.097

	Tert-butylamine	N-Methylaniline	Cyclohexylamine	Ammonia	Ethylamine
τ_{Tb} (τ_{Tb}') /ms	0.291	0.217	0.240	0.015	0.015
lnk_{back}/s^{-1}	6.389	7.473	7.184	11.064	11.064

	Propylamine	1,3-Propanediamine,	Methylamine	Ethylenediamine
τ_{Tb} (τ_{Tb}') /ms	0.038	0.018	0.015	0.020
lnk_{back}/s^{-1}	10.063	10.872	11.064	10.761

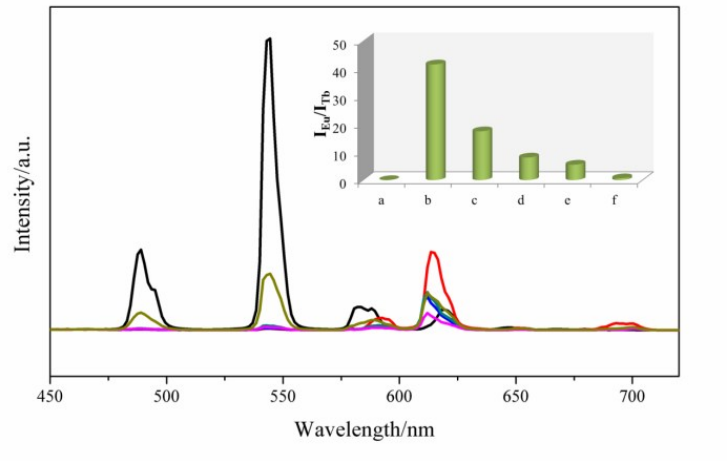


Figure S7 Emission spectra of $Eu_{0.5}Tb_{9.5}(HFA)_n$@ZY after treatment with several amine vapors using an excitation wavelength of 302 nm. ($Eu_{0.5}Tb_{9.5}(HFA)_n$@ZY (black line), ammonia (red line), Propylamine (blue line), Butylamine (cyan line), 1,3-Propanediamine (magenta line), Benzylamine (orange line)). Inset: The relative emission intensity at 612 nm and at 544 nm (I_{Eu}/I_{Tb}) of $Eu_{0.5}Tb_{9.5}(HFA)_n$@ZY excited at 302 nm upon treatment with several amine solvent vapors. (a: $Eu_{0.5}Tb_{9.5}(HFA)_n$@ZY, b: ammonia, c: Propylamine, d: Butylamine, e: 1,3-Propanediamine, f: Benzylamine).

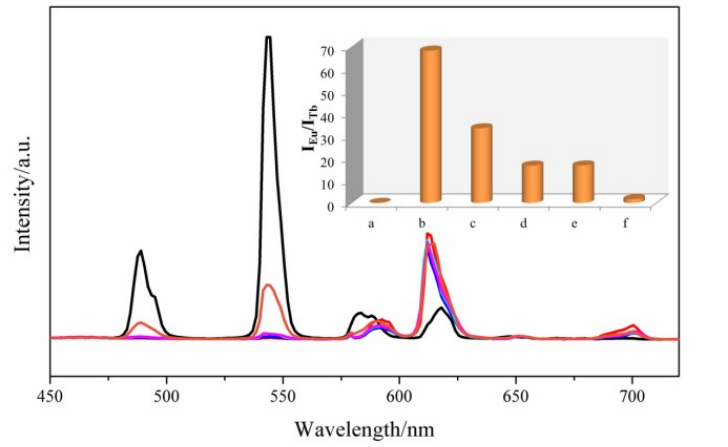


Figure S8 Emission spectra of $Eu_1Tb_9(HFA)_n$@ZY after treatment with several amine vapors using an excitation wavelength of 302 nm. ($Eu_1Tb_9(HFA)_n$@ZY (black line), ammonia (red line), Propylamine (blue line), Butylamine (cyan line), 1,3-Propanediamine (magenta line), Benzylamine (orange line)). Inset: The relative emission intensity at 612 nm and at 544 nm (I_{Eu}/I_{Tb}) of $Eu_1Tb_9(HFA)_n$@ZY excited at 302 nm upon treatment with several amine solvent vapors. (a: $Eu_{0.5}Tb_{9.5}(HFA)_n$@ZY, b: ammonia, c: Propylamine, d: Butylamine, e: 1,3-Propanediamine, f: Benzylamine).

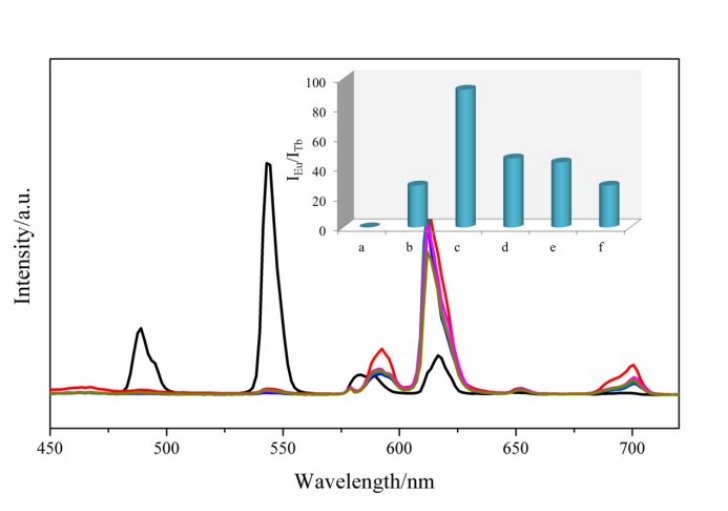


Figure S9 Emission spectra of $Eu_2Tb_8(HFA)_n$@ZY after treatment with several amine vapors using an excitation wavelength of 302 nm. ($Eu_2Tb_8(HFA)_n$@ZY (black line), ammonia (red line), Propylamine (blue line), Butylamine (cyan line), 1,3-Propanediamine (magenta line), Benzylamine (orange line)). Inset: The relative emission intensity at 612 nm and at 544 nm (I_{Eu}/I_{Tb}) of $Eu_2Tb_8(HFA)_n$@ZY excited at 302 nm upon treatment with several amine solvent vapors. (a: $Eu_{0.5}Tb_{9.5}(HFA)_n$@ZY, b: ammonia, c: Propylamine, d: Butylamine, e: 1,3-Propanediamine, f: Benzylamine).

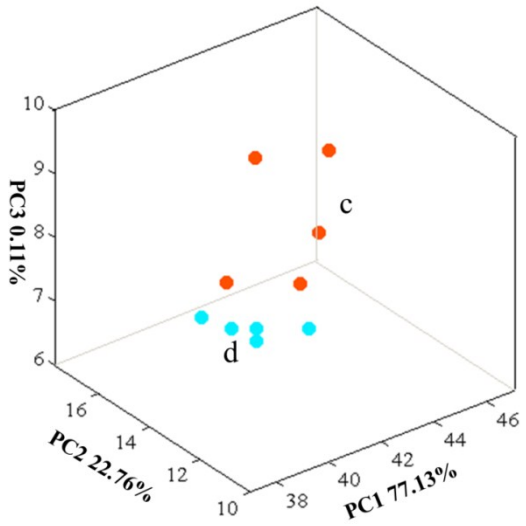


Figure S10 The enlarged three dimensional PCA score plot for c (Butylamine) and d (1,3-Propanediamine) derived from the luminescence data.

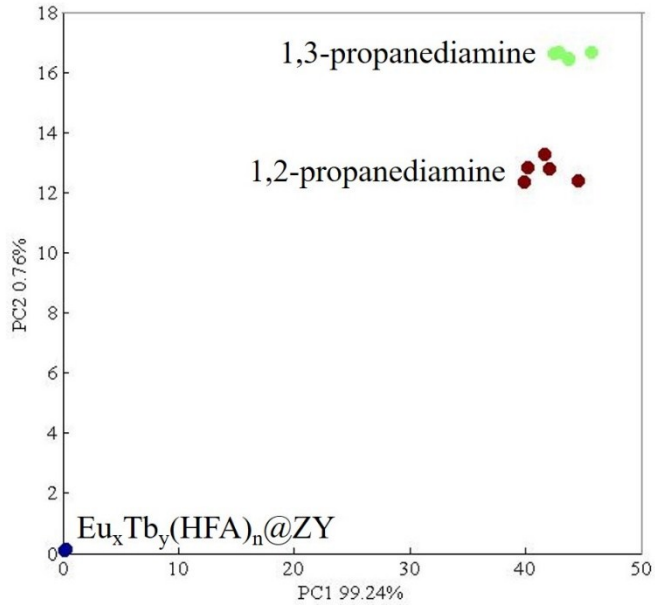


Figure S11 The two dimensional PCA score plot for 1'2-propylenediamine/1'3-propylenediamine derived from the luminescence data.

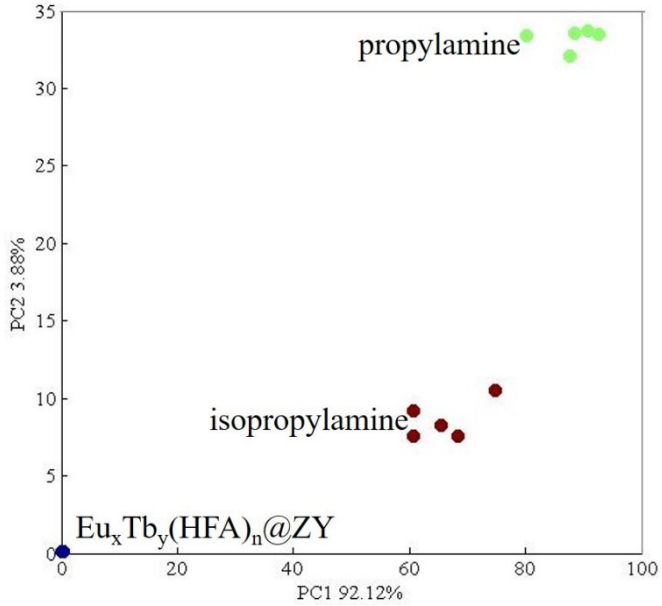


Figure S12 The two dimensional PCA score plot for propylamine/isopropylamine derived from the luminescence data.

Notably, the sensor array can achieve the identification of two sets of isomers through two dimensional PCA score plot for 1'2-propylenediamine/1'3-propylenediamine derived from the luminescence data.

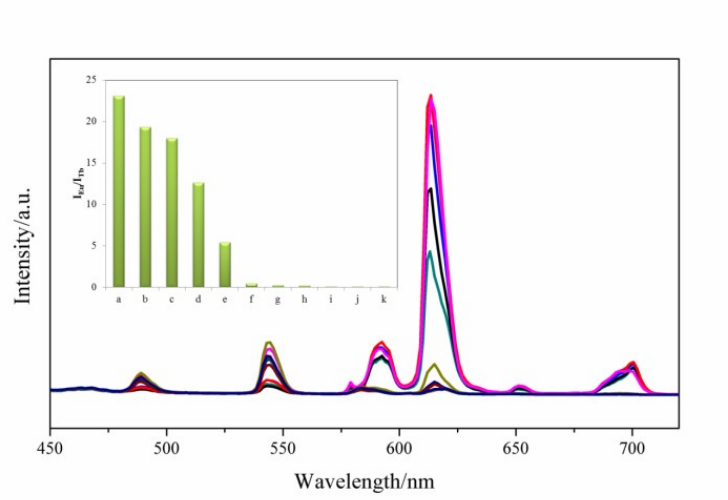


Figure S13 Emission spectra of $Eu_{0.5}Tb_{9.5}(HFA)_n$@ZY after treatment with ammonia solution with different concentrations using an excitation wavelength of 302 nm. (2.5×10^{-1} v/v (black line), 5×10^{-2} v/v (red line), 1×10^{-2} v/v (blue line), 2×10^{-3} v/v (dark cyan line), 4×10^{-4} v/v (magenta line), 2×10^{-4} v/v (dark yellow line), 1×10^{-4} v/v (navy line), 8×10^{-5} v/v (80 ppm) (wine line), 1.6×10^{-5} v/v (pink line), 3.2×10^{-6} v/v (olive line), 0 (royal line))). Inset: The relative emission intensity at 612 nm and at 544 nm (I_{Eu}/I_{Tb}) of $Eu_{0.5}Tb_{9.5}(HFA)_n$@ZY excited at 302 nm upon treatment with ammonia solution with different concentrations. (ammonia concentration in H_2O: a: 2.5×10^{-1} v/v, b: 5×10^{-2} v/v, c: 1×10^{-2} v/v, d: 2×10^{-3} v/v, e: 4×10^{-4} v/v, f: 2×10^{-4} v/v, g: 1×10^{-4} v/v, h: 8×10^{-5} v/v (80 ppm), i: 1.6×10^{-5} v/v, j: 3.2×10^{-6} v/v , k:0).

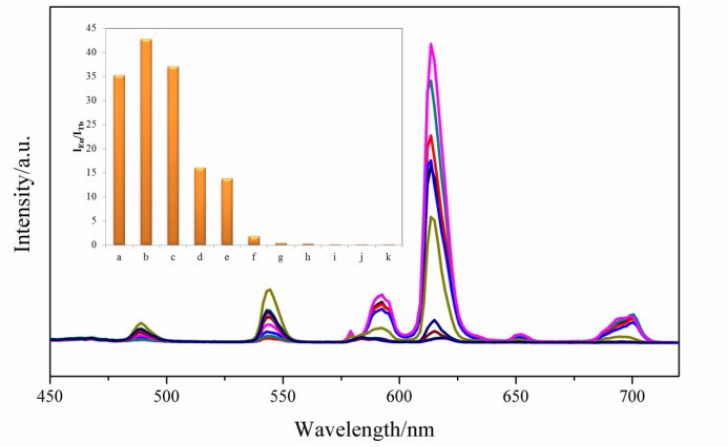


Figure S14 Emission spectra of $Eu_1Tb_9(HFA)_n$@ZY after treatment with ammonia solution with different concentrations using an excitation wavelength of 302 nm. (2.5×10^{-1} v/v (black line), 5×10^{-2} v/v (red line), 1×10^{-2} v/v (blue line), 2×10^{-3} v/v (dark cyan line), 4×10^{-4} v/v (magenta line), 2×10^{-4} v/v (dark yellow line), 1×10^{-4} v/v (navy line), 8×10^{-5} v/v (80 ppm) (wine line), 1.6×10^{-5} v/v (pink line), 3.2×10^{-6} v/v (olive line), 0 (royal line))). Inset: The relative emission intensity at 612 nm and at 544 nm (I_{Eu}/I_{Tb}) of $Eu_1Tb_9(HFA)_n$@ZY excited at 302 nm upon treatment with ammonia solution with different concentrations. (ammonia concentration in H_2O: a: 2.5×10^{-1} v/v, b: 5×10^{-2} v/v, c: 1×10^{-2} v/v, d: 2×10^{-3} v/v, e: 4×10^{-4} v/v, f: 2×10^{-4} v/v, g: 1×10^{-4} v/v, h: 8×10^{-5} v/v (80 ppm), i: 1.6×10^{-5} v/v, j: 3.2×10^{-6} v/v , k:0).

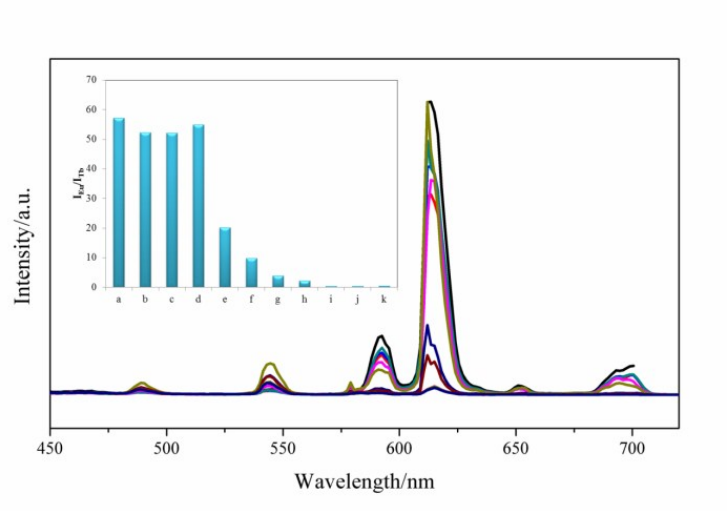


Figure S15 Emission spectra of $Eu_2Tb_8(HFA)_n$@ZY after treatment with ammonia solution with different concentrations using an excitation wavelength of 302 nm. (2.5×10^{-1} v/v (black line), 5×10^{-2} v/v (red line), 1×10^{-2} v/v (blue line), 2×10^{-3} v/v (dark cyan line), 4×10^{-4} v/v (magenta line), 2×10^{-4} v/v (dark yellow line), 1×10^{-4} v/v (navy line), 8×10^{-5} v/v (80 ppm) (wine line), 1.6×10^{-5} v/v (pink line), 3.2×10^{-6} v/v (olive line), 0 (royal line))). Inset: The relative emission intensity at 612 nm and at 544 nm (I_{Eu}/I_{Tb}) of $Eu_2Tb_8(HFA)_n$@ZY excited at 302 nm upon treatment with ammonia solution with different concentrations. (ammonia concentration in H_2O: a: 2.5×10^{-1} v/v, b: 5×10^{-2} v/v, c: 1×10^{-2} v/v, d: 2×10^{-3} v/v, e: 4×10^{-4} v/v, f: 2×10^{-4} v/v, g: 1×10^{-4} v/v, h: 8×10^{-5} v/v (80 ppm), i: 1.6×10^{-5} v/v, j: 3.2×10^{-6} v/v , k:0).

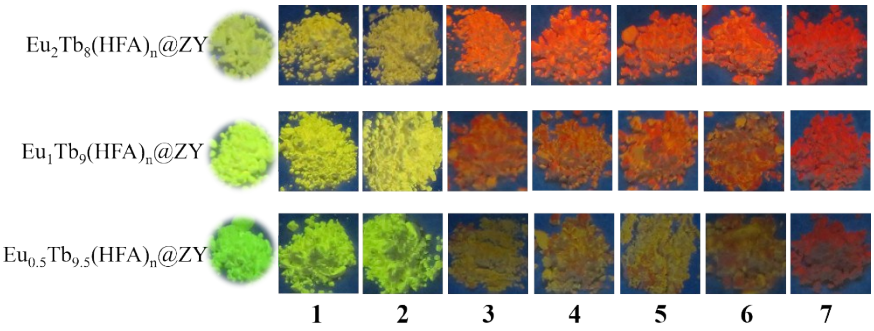


Figure S16 Digital photographs of $Eu_xTb_y(HFA)_n$@ZY upon exposed to various volume concentration of 1,3-propanediamine in trimethylamine and 1,3-propanediamine mixed solvents for 5 min (for more sufficient reaction) under near UV irradiation at 302 nm. (the volume concentration of 1,3-propanediamine: **1:** 0, **2:** 5×10^{-4} v/v, **3:** 1×10^{-3} v/v, **4:** 2.5×10^{-3} v/v, **5:** 5×10^{-3} v/v, **6:**0.8 v/v, **7:** 1)

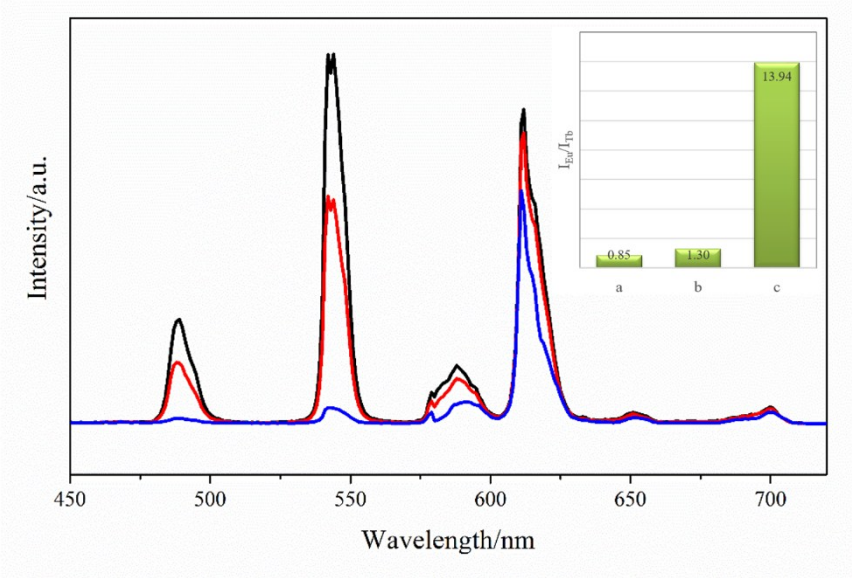


Figure S17 Emission spectra of $Eu_2Tb_8(HFA)_n$@ZY after treatment with different volume concentration of 1,3-propanediamine in trimethylamine and 1,3-propanediamine mixed solvents for 5 min. (trimethylamine: black line, 5×10^{-4} v/v**:** red line and 1×10^{-3} v/v: blue line). Inset: The relative emission intensity at 612 nm and at 544 nm (I_{Eu}/I_{Tb}) of $Eu_2Tb_8(HFA)_n$@ZY excited at 302 nm upon treatment with ammonia solution with volume concentration of 1,3-propanediamine in trimethylamine and 1,3-propanediamine mixed solvents for 5 min. (a: trimethylamine, b: 5×10^{-4} v/v and c: 1×10^{-3} v/v).

Notably, the single sensing element such as $Eu_2Tb_8(HFA)_n$@ZY can accomplish the identification of lower concentration of 1,3-propanediamine in trimethylamine and 1,3-propanediamine mixed solvents.

Table S2 The equilibrated vapor pressure of 1,3-propanediamine in trimethylamine.

	trimethylamine	1,3-propanediamine
Saturated vapor pressure(KPa)	9.06	<1.07

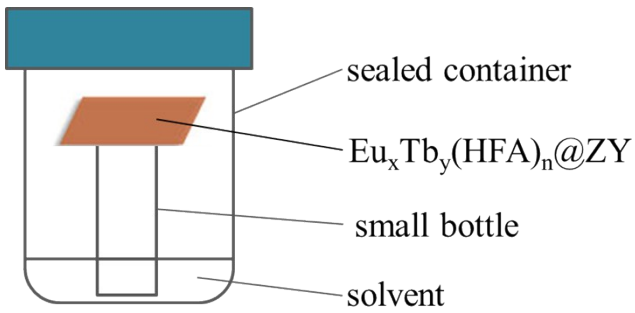
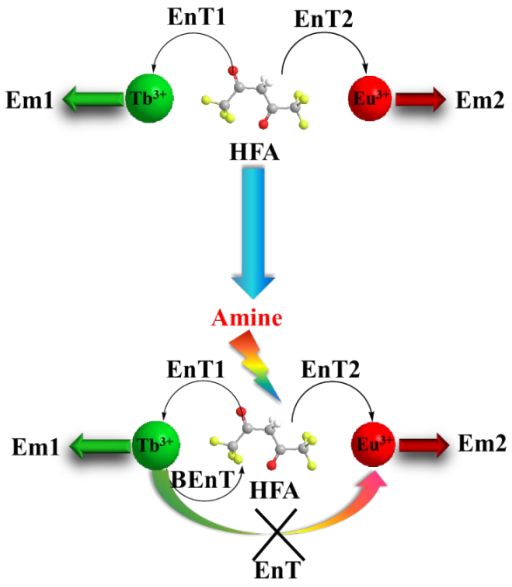


Figure S18 Diagram of the experimental setup for exposing $Eu_xTb_y(HFA)_n$@ZY to various amine solvent vapors.



Scheme S1 Detailed process of energy transfer from ligand HFA to Tb^{3+} and Eu^{3+} with the stimulation of amine vapors (EnT: energy transfer, BEnT: energy back transfer).