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Electronic Supporting Information

For

Paper-based lanthanide smart device for acid-base vapours detection, anti-counterfeiting and logic operations

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Contents

1. Experimental Methods

1.1 Synthesis of N-(2-pyridinyl)benz-oylacetamide (HPBA)

The photosensitizer N-(2-pyridinyl)benzoylacetamide (HPBA) was synthesized according to a process described previously.[S1] The synthesis of HPBA is shown in Scheme S1. A portion of ethyl benzoylacetate (21.12 g, 0.11 mol) and 2-aminopyridine (4.7 g, 0.05 mol) was added into a 250 mL round bottom flask which contained about 70 mL xylene. The reaction mixture was stirred magnetically and refluxed at 135 °C until the colour turned to canary yellow. Then the mixture was transferred into a 150 mL beaker immediately and cooled down naturally. Petroleum ether (40 mL) was added into this beaker after observing the precipitation of crystals. After vacuum distillation, the obtained white solid powder was washed three times with benzene-petroleum ether (v/v=1:1) and dried at 50 °C under vacuum. Yield: 8.761 g（73%); m.p. 105-110 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) : 4.16 (s, 2 H), 7.26 (t, 1H), 7.48 (t, 2H), 7.52 (t, 1H), 7.74 (t, 1H), 8.20 (d, 2H), 8.24 (d, H), 8.63 (d, 1H), 9.93 (s, 1H); Elemental analysis calcd (%) for $C_{14}H_{12}N_2O_2$: C 69.89, H 4.92, N 11.58; found: C 69.99, H 5.03, N 11.66; MS: $m/z = 241.09\ [M + H]^+$， $m/z = 263.07\ [M + Na]^+$.

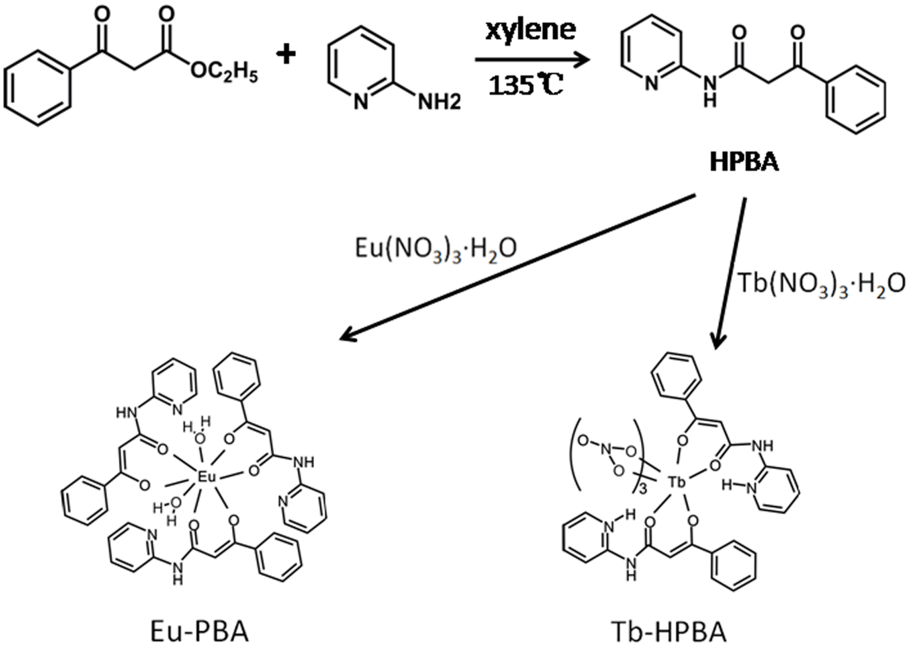
1.2 Synthesis of [$Tb(HPBA)_2(NO_3)_3$] (Tb-HPBA), [$Gd(HPBA)_2(NO_3)_3$] (Gd-HPBA)

Following a previously described procedure,[S1] $Tb(NO_3)_3\cdot 6H_2O$ (45.30 mg, 0.1 mmol) or $Gd(NO_3)_3\cdot 6H_2O$ (45.14 mg, 0.1 mmol) and HPBA (72.03 mg, 0.3 mmol) were dissolved in ethyl acetate (2 mL) or in chloroform (2 mL) respectively. Under magnetic stirring, both solutions were filtered into the round bottom flask successively. Then the obtained mixture was stirred at room temperature for 4 h and centrifuged. The precipitated canary yellow solid was washed three times with a mixture of ethyl acetate and chloroform (v/v=1:1) and then dried in vacuo over P_4O_{10} for 48 hours to obtain Tb-HPBA and Gd-HPBA. Elemental analysis (%) calc. (found) for

$[Tb(HPBA)_2(NO_3)_3]\cdot CH_3CO_2C_2H_5$: C, 42.01 (41.84); H, 3.43 (3.48); N, 10.63 (10.55). MS: m/z = 826.18 $[Tb(HPBA)_2(NO_3)_3 + 1]^+$. Elemental analysis (%) calc. (found) for $[Gd(HPBA)_2(NO_3)_3]\cdot CH_3CO_2C_2H_5$: C, 42.15 (42.31); H, 3.54 (3.47); N, 10.75 (10.79). MS: m/z = 824.18 $[Gd(HPBA)_2(NO_3)_3 + 1]^+$. The crystal structure of an analogous complex has been reported by our group.[S2]

1.3 Synthesis of $[Eu(PBA)_3(H_2O)_2]$ (Eu-PBA)

$Eu(NO_3)_3\cdot 6H_2O$ (44.61 mg, 0.1 mmol) and HPBA (72.03 mg, 0.3 mmol) were dissolved in water (2 mL) or in ethanol (2 mL) respectively. An appropriate amount of 1.0 M sodium hydroxide aqueous solution was added dropwise to the HPBA ethanol solution under stirring to adjust the pH value to slightly alkaline conditions（pH ≈ 8）. Under magnetic stirring, both solutions were filtered into the round bottom flask successively. Then the obtained mixture was stirred at room temperature for 4 h and centrifuged. The precipitated canary yellow solid was washed three times with a mixture of ethyl acetate and chloroform (v/v=1:1) and then dried in vacuo over P_4O_{10} for 48 hours to obtain Eu-PBA. MS: m/z = 871.18 $[Eu(PBA)_3 + 1]^+$. Elemental analysis (%) calc. (found) for $[Eu(PBA)_3(H_2O)_2]\cdot CH_3CH_2OH$: C, 55.63 (55.77); H, 4.61 (4.66); N, 8.89 (8.97).



Scheme1. Synthetic route to HPBA, Eu-PBA and Tb-HPBA.

2. Supporting Figures

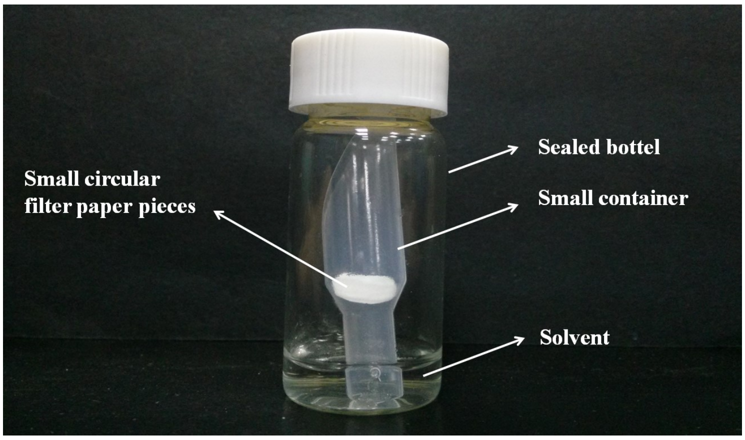


Fig. S1 Digital photograph of the experimental setup for exposing paper-based sensor to different solvent, acid or base vapours.

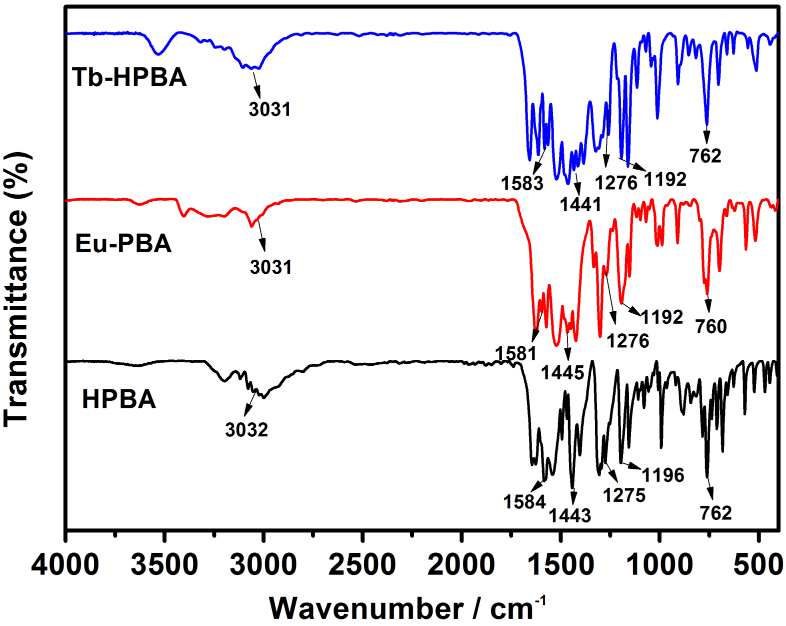


Fig. S2 FTIR spectra of HPBA, Eu-PBA and Tb-HPBA.

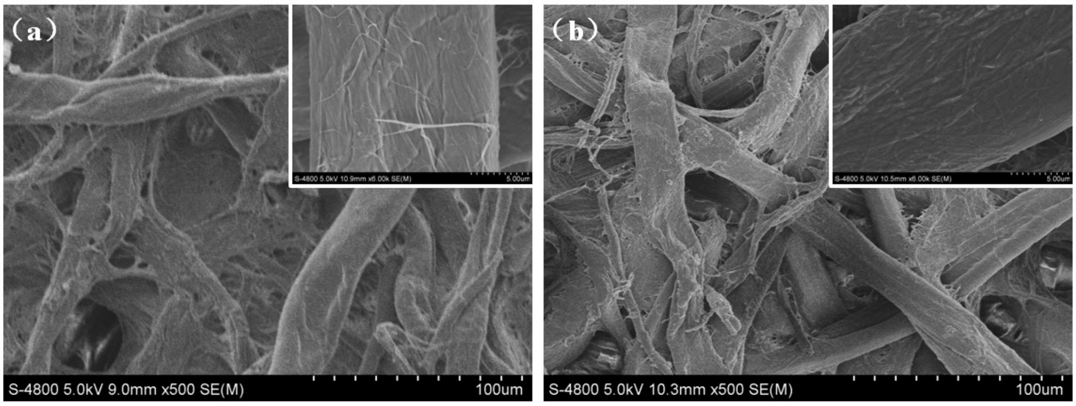


Fig. S3 SEM image of the filter paper (a) before and (b) after the impregnation with Eu-PBA or Tb-HPBA; Scale bar: 100 μm. The inset shows a higher resolution images; Scale bar: 5 μm.

Table S1 The excited state $^5D_4$ lifetimes and the absolute quantum yields of Tb-HPBA and Paper-Tb, as well as the excited state $^5D_0$ lifetimes and the absolute quantum yields of Eu-PBA and Paper-Eu.[a]

Sample	**τ_1 (μs)**	**τ_2 (μs)**	**τ_{avg} (μs)**	**Q(%)**
Eu-PBA	336.27 (100%)	——	336.27	7.2
Paper-Eu	138.57 (37.5%)	364.04 (62.50%)	322.12	6.6
Tb-HPBA	151.25 (100%)	——	151.25	2.8
Paper-Tb	144.06 (23.35%)	558.4 (76.65%)	528.21	7.4

[a] Lifetimes (τ) and corresponding relative weightings (A), average lifetimes τ_{avg}. [b] Calculated using the equation $\tau_{avg} = \sum A_i \tau_i^2 / \sum A_i \tau_i$.[S3] [c] The absolute quantum yields Q.

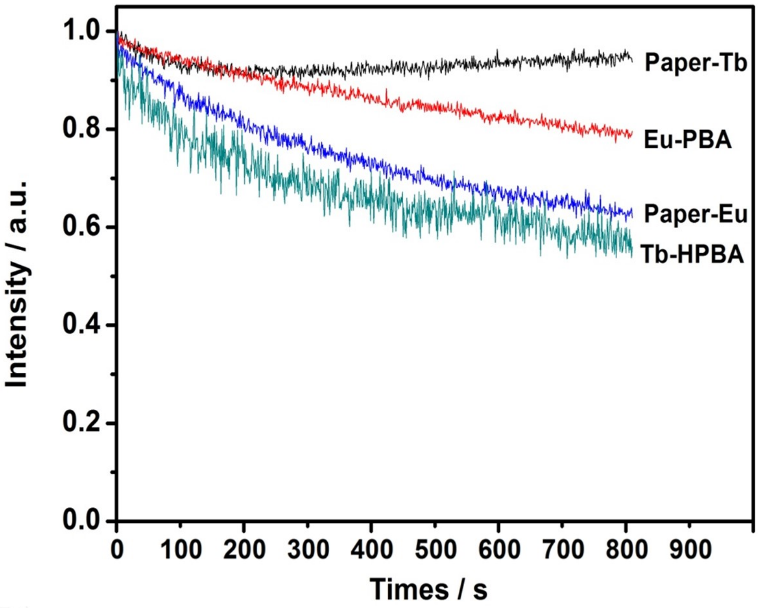


Fig. S4 Photoluminescence stabilities of Tb-HPBA and Paper-Tb (normalized intensities of the $^5D_4 \rightarrow {}^7F_5$ transition as a function of time) and of Eu-PBA and Paper-Eu (normalized intensities of the $^5D_0 \rightarrow {}^7F_2$ transition as a function of time).

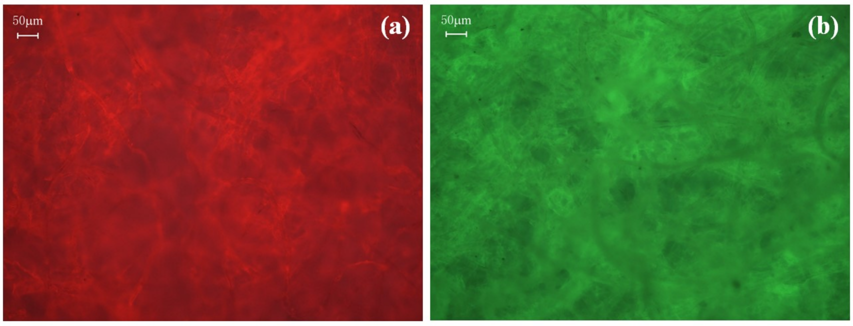


Fig. S5 Fluorescence microscopy images of (a) Paper-Eu and (b) Paper- Tb; Scale bar: 50 μm.

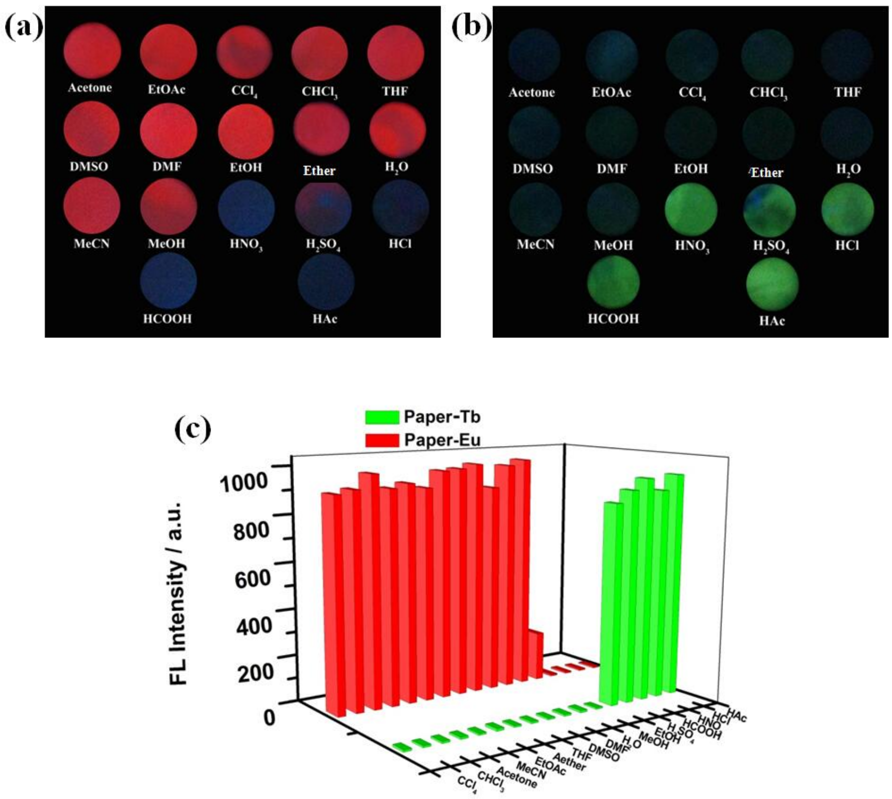


Fig. S6 Fluorescent response of (a) Paper-Eu and (b) Paper-Tb after the exposure to vapours of various acids and common organic solvents. (a, b) Digital phototographs were taken under the 365 nm UV irradiation. (c) Fluorescent changes in the emission intensity of the $^5D_0 \rightarrow ^7F_2$ transition at 613 nm (Paper-Eu) and the $^5D_4 \rightarrow ^7F_5$ transition at 545 nm (Paper-Tb).

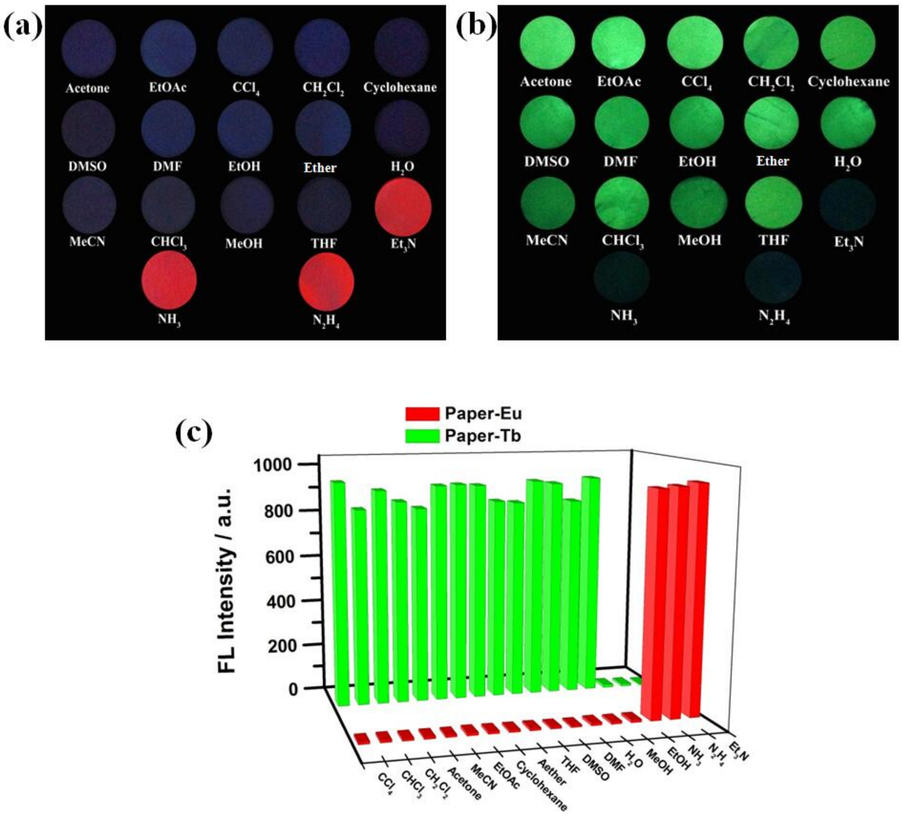


Fig. S7 Fluorescent response of (a) Paper-Eu and (b) Paper-Tb after the exposure to vapours of various bases and common organic solvents. (a, b) Digital phototographs were taken under the 365 nm UV irradiation. (c) Fluorescent changes in the emission intensity of the $^5D_0 \rightarrow {}^7F_2$ transition at 613 nm (Paper-Eu) and the $^5D_4 \rightarrow {}^7F_5$ transition at 545 nm (Paper-Tb).

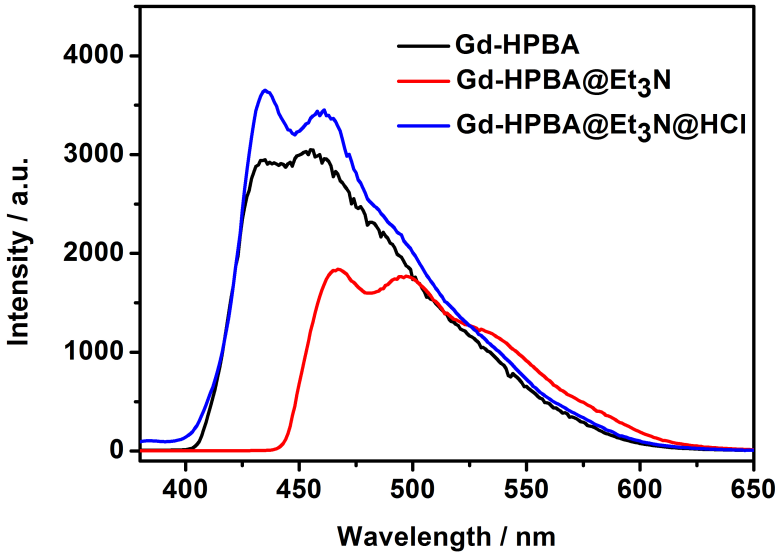


Fig. S8. Phosphorescence spectra of Gd-HPBA (black), Gd-HPBA after the treatment with the Et_3N vapour (red), and Gd-HPBA after the treatment with the HCl gas (blue); spectra were measured in a 1:1 methanol-ethanol mixed solution.

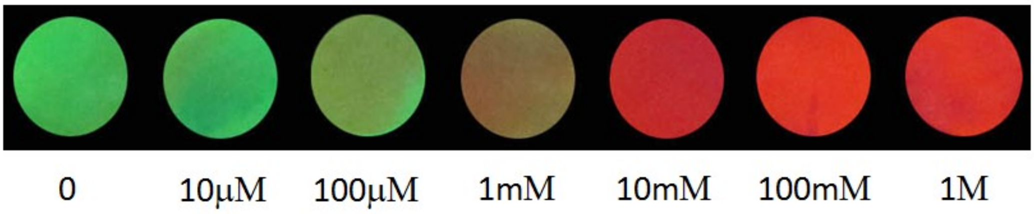


Fig. S9 Digital photographs of Paper-Eu/Tb in the presence of 0 μM, 10 μM, 100 μM, 1 mM, 10 mM, 100 mM, and 1 M of triethylamine under the UV light illumination.

3. Supporting References

[S1] J. Xu, L. Jia, N. Z. Jin, Y. F. Ma, X. Liu, W. Y. Wu, W. S. Liu, Y. Tang and F. Zhou, Chem. Eur. J., 2013, **19**, 4556.

[S2] L. Xu, K. Z. Tang, Y. Tang, M. Y. Tan, Anal. Sci., 2007, **23**, X71-X72.

[S3] V. M. Martínez, F. L. Arbeloa, J. B. Prieto, I. L. Arbeloa, J. Phys. Chem. B., 2005, **109**, 7443-7450.