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A simple photoluminescent strategy for pH and amine vapors detection based on Eu(III)-complex functionalized material

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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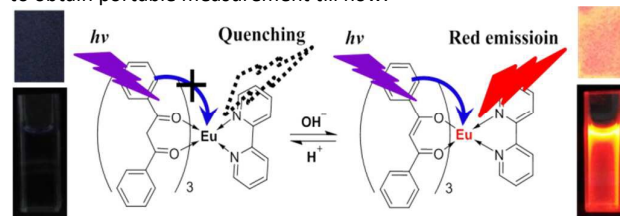
In this work, we report the development of easy-prepared, low cost and portable photoluminescent films for pH and amine vapors detection based on Eu(III)-complex functionalized materials: Eu(DBM)₃Phen (LMOF-1), Eu(DBM)₃BPY (LMOF-2), which were loaded on portable matrices (e.g. neutral silica plate and normal filter paper). The films not only displayed response over a pH range of 4-13 but also can be employed to sense volatile amines or acids vapors like ammonia, ethylenediamine, acetic acid and hydrochloric acid etc., which is significant for portable pH or acid-base vapors detection.

Introduction

Lanthanide-based metal organic frameworks (LMOFs) not only have the characteristics of both organic and inorganic compounds, but also have many unique properties such as electron transfer,¹ porous structures and characteristic emissions.² Lanthanide-based luminescent probes have more excellent performances than organic fluorophores for their atomic-based narrow emissions (<30 nm bandwidth),³ large Stokes shifts (>150 nm) and long luminescence lifetimes (ms),⁴ leading to more and more applications.^{5, 6} The solution-based LMOFs photoluminescence detection displays the intrinsic shortcomings of inconvenient to store and transport,⁷ causing wastes and pollution with one-off detection,^{8, 9} hard to sense vapors/gases^{10, 11} and unstable in aqueous solution.¹² To overcome these deficiencies, some LMOFs-based functional hybrid material films have been exploited. For example, Eu(III)- β -diketonate complex nano-hybrid laponite¹³ and upconversion hybrid luminescent film¹⁴ have been reported for pH detection, and these hybrid materials have good reversibility after many times cycles and provide high reliability and fast response. Eu(III)-coordination polymer¹⁵ and Eu(III)- β -diketonate hybrid functionalized films^{16, 17} have been developed for amine vapor detection. Compared with the luminescent testing based on probes in solution, luminescent materials have changeable shape,^{18, 19} more stable performance,²⁰ convenient and non-invasive detection in real-time.²¹ Unfortunately, most of the films contain pretty much rare earth elements,^{22, 23} have complicated preparing process and cannot be mass-produced,^{24, 25} bear lower responsive sensitivity to

stimulus²⁶ and poorly mechanical characteristics.²⁷ Therefore, developing new methods for preparing thin film materials is still of great importance.^{28, 29}

According to the literature,³⁰ the β -diketonate-based ligand DBM (DBM=1,3-diphenylpropane-1,3-dione) has the conformational transformation between enol and keto form in different acid-base environment. Both Phen (Phen=1,10-phenanthroline) and BPY (BPY=2,2'-Dipyridine) have pyridine moiety and can be protonated and de-protonated under stronger acidic and alkalic circumstance,³¹⁻³⁴ respectively. The changes of these ligands would affect the coordination of LMOFs and then influence the characteristic emission of Eu(III) in the end. Especially, Phen has stronger rigid structure than BPY due to the two pyridine rings linked by benzene, and BPY has more flexible conformation owing to the rotatable C₂-C₂' bond.^{35, 36} So BPY has a relatively smaller chelate cave and higher binding ability than Phen to Eu(III).³⁷ Considering of these, Eu(DBM)₃Phen (LMOF-1) was synthesized to make a comparison with Eu(DBM)₃BPY (LMOF-2) in this paper (Scheme S1). Although the two complexes have been reported,^{38, 39} to the best of our knowledge, there has been no reports for loading them onto matrices like neutral silica plate and normal filter paper to obtain portable measurement till now.



Scheme 1. Response mechanism of the LMOF-2 to acid-base changes.

Hence, a simple luminescent sensing strategy has been designed for pH and amine vapors detection after loading LMOF-1, LMOF-2 on portable matrices such as neutral silica plate and normal filter paper (Scheme 1 and Scheme S2). The easy-prepared sensor not only displayed response over a pH range of 4-13 in the solution of

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† Electronic Supplementary Information (ESI) available: Additional NMR, MS, FT-IR, UV-vis. SEM and luminescence spectra. See DOI: 10.1039/x0xx00000x

H₂O/DMSO (v/v=5/1) but also can be employed to sense volatile amines or acids vapors like ammonia, ethylenediamine, acetic acid and hydrochloric acid etc., which is significant for portable pH or acid-base vapors detection.

Experimental section

Materials and instruments

All the chemicals used were analytical grade and purchased from commercial sources unless specifically noted. Europium (III) chloride hexahydrate (99.99 %) was purchased from Jining Zhongkai New Type Material Science Co, Ltd (China). The ligands DBM, Phen and BPY were purchased from Aladdin (China). Other chemicals and solvents were purchased from China National Medicine Group. ¹H NMR and ¹³C NMR spectra were obtained using a Bruker 500 avance III spectrometer (Germany). Tetramethylsilane (TMS) was used as the internal standard to report the chemical shifts (δ). Mass spectrometric (MS) data were obtained with HP1100LC/MSD MS and LC/Q-TOF-MS instruments (USA). Fourier transform infrared spectra (FTIR) were measured by Bruker Tensor 27 FTIR spectrometer (Germany). A Quanta 200 environmental scanning electron microscope (SEM) was used to observe the morphologies of the obtained materials. The pH value in this study was determined by a PHS-3C pH Meter (China). The UV-vis spectra were recorded on a Shimadzu 1750 UV-visible spectrometer (Japan). And the emission and excitation spectra were performed on a FR-5301 fluorescence spectrometer (Japan).

Synthesis of LMOF-1 and LMOF-2

The complexes LMOF-1 and LMOF-2 were prepared according to the previously reported procedure.⁴⁰ LMOF-1: ¹H NMR (500 MHz, Acetone-*d*₆): δ 11.84 (s, 2H), 11.21 (d, *J* = 6.3 Hz, 2H), 10.63 (s, 2H), 9.33 (d, *J* = 7.9 Hz, 2H), 6.87 (s, 18H), 6.32 (s, 12H), 3.34 (s, 3H). ¹³C NMR (125 MHz, Acetone-*d*₆): δ 182.16, 171.60, 168.24, 152.01, 132.35, 130.45, 125.79, 125.76, 118.04, 111.60, 93.90, 60.97. ESI-MS (*m/z*): 1025.67 for [M+Na]⁺. LMOF-2: ¹H NMR (500 MHz, CDCl₃): δ 13.13 (s, 2H), 11.38 (s, 2H), 9.94 (s, 2H), 8.87 (s, 2H), 6.88 (s, 18H), 6.35 (s, 12H), 3.12 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 172.76, 166.43, 155.29, 149.35, 131.00, 128.76, 125.04, 124.82, 121.61, 93.51, 60.15. ESI-MS (*m/z*): 1000.37 for [M+Na]⁺.

Physical characterization

The FTIR of Phen, DBM, LMOF-1, BPY and LMOF-2 were recorded by using KBr pellets for solid samples from 4000 to 400 cm⁻¹. UV-vis spectra of DBM (30 μ M), Phen (12 μ M), BPY (40 μ M), LMOF-1 (8 μ M) and LMOF-2 (10 μ M), excitation and emission spectra of LMOF-1 and LMOF-2 were all recorded in mixed solution of H₂O/DMSO (V/V=5/1).

Preparation of the functionalized films

5 mL water containing PVA (Poly vinyl alcohol, 4.4 mg) was added to 200 mL solution (CH₂Cl₂/MeOH, V/V=1/1) of LMOF-1 (5.0 mg) or LMOF-2 (8.0 mg) under sonication to get a mixture solution. Filter papers or silica plates (1.1 \times 2 cm²) were dipped into the solution and ultrasonic processed for few minutes. Then taken them out and dried in the air to get LMOFs-based functionalized papers or silica plates. Detailed process was shown in Fig. S15.

Recorded the emission and absorption spectra of LMOFs in different pH solution

Various solutions of different pH values (pH values: 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, 12.0, 12.5 and 13.0) were prepared for the pH detection. Then 12 μ L 2 mM LMOF-1 or 6 μ L 5 mM LMOF-2 was added to 3 mL mixed solution with pH solution/DMSO (V/V=5/1) to test their absorbance and photoluminescence properties, respectively.

Detection pH and vapors with the prepared films

As shown in Fig. S17, the setups were designed¹⁵ so as to test photoluminescence properties of the prepared papers during diverse pH solution and organic vapor environment. The prepared papers (1.1 \times 2 cm²) were immersed into different pH solution for 10 min, then took out and put into quartz cuvette (1 \times 1 \times 4.5 cm³) along the diagonal direction to measure their photoluminescence. Then the photos were taken under UV light (365 nm) for the corresponding tested papers.

To measure the photoluminescence response of the films to vapors, 50 μ L various samples were added to the small vessel carefully. The films were suspended on the sample with the cap covered for 15 min, and then their emission spectra were recorded by fluorescence spectrometer. And the pictures were taken under UV light (365 nm) after the films treated by vapors.

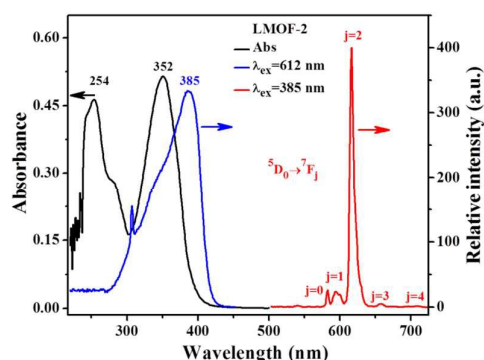


Fig. 1 The absorption, excitation and emission spectra of LMOF-2 (10 μ M) in mixed solution (H₂O/DMSO, v/v=5/1).

Results and discussion

Synthesis and characterization of LMOF-1 and LMOF-2

The ESI-MS spectra with positive mode revealed that LMOF-1 with a Na⁺ was 1025.67, and LMOF-2 with a Na⁺ was 1000.37 (Fig. S3 and S6). All the chemical shifts of the protons were assigned to the definite region and in good agreement with the NMR data reported in literature.⁴¹ The coordination of Eu(III) and the ligands was further examined by FT-IR spectroscopy (Fig. S7 and S8).⁴² The absorption band at 2076 cm⁻¹ disappeared after forming Eu(III)- β -diketone complex LMOFs, which was assigned to the vibration of C-O in enol form of β -diketone.⁴³ Moreover, a new peak occurred at 512 cm⁻¹ attributed to Eu-O from LMOF-1 and LMOF-2.⁴⁴ The absorption bands at 1600, 1537 cm⁻¹ were ascribed to the C=O and C=C in DBM, which shifted to 1596, 1516 cm⁻¹ in the LMOFs.²³ The morphologies of LMOF-1 and LMOF-2 were observed by SEM. As

shown in Fig. S24 and S25, different morphologies of LMOF-1 and LMOF-2 were observed in the condition of different pH values, which can be ascribed to the conformational transformation between enol and keto form in different acid-base environment³⁰ and protonation and deprotonation of Phen and BPY under stronger acidic and alkalic circumstance.³¹⁻³⁴ In acidic environment, LMOFs was damaged and no crystal can generate (Fig. S24a and S25a) owing to the protonation of Phen and BPY as well as the ketonic transformation of DBM. However, along with the increase of pH value, crystal generated gradually, from block to strip (Fig. S24b-d and S25b-d).

The absorption spectra of all the ligands and two LMOFs indicated that Phen had a characteristic absorption peak at 265 nm, DBM at 252 and 348 nm, LMOF-1 at 258 and 349 nm, BPY at 284 nm, LMOF-2 at 254, 282 and 352 nm, respectively (Fig. S10 and S12). When excited at $\lambda_{ex}=373$ nm (LMOF-1) and $\lambda_{ex}=385$ nm (LMOF-2), both LMOF-1 and LMOF-2 exhibited the characteristic emission at 579, 590, 612, 653 and 705 nm from the $^5D_0 \rightarrow ^7F_j$ ($j=0,1,2,3,4$) transitions of Eu(III), among them, the strongest and sharp emission was at 612 nm (Fig. 1 and S11).

Luminescence changed of LMOFs in pH solution

The luminescence of LMOF-2 (Fig. 2) was completely quenched with the pH values varied from 3.0 to 3.5. However, the luminescence enhanced gradually with the pH values increased from 4.0 to 11.5. And the detection exhibited wide linear range and fine linear correlation. The luminescence intensity decreased slowly when the pH value increased from 11.5 to 13.0 owing to the generation of Eu(III)-hydroxide precipitates. All these can be attributed to the coordination ability change of the ligands to Eu(III) under different pH. In comparison, LMOF-1 displayed poorer pH response than that of LMOF-2 (Fig. S13).

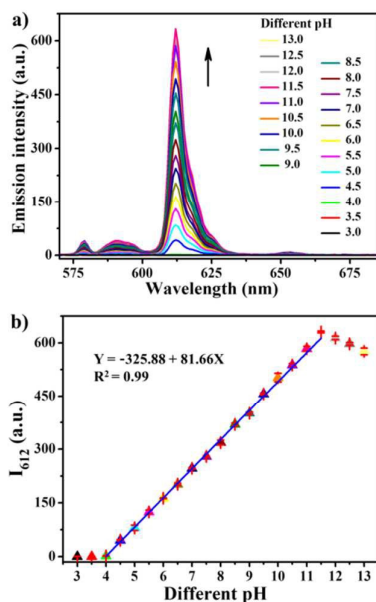


Fig. 2. a) The emission spectra changes of LMOF-2 (10 μ M) under different pH conditions ($H_2O/DMSO$, $v/v=5/1$, $\lambda_{ex}=385$ nm). b) The relationship between the emission intensity at 612 nm and the pH changes from 3.0 to 13.0.

Response mechanism of LMOFs to pH

The detecting processes of two LMOFs in different pH solution were verified by absorption spectra. The absorption of LMOF-2 (Fig. 3) at 352 nm demonstrated no significant changes but slightly red shift with the pH changes from 3.0 to 11.5. The absorption at 303 nm appeared distinct decrease with the pH increments from 3.5 to 4.0, due to the transformation from enol to keto tautomer of DBM and protonation of $N_{Pyridyl}$ in strong acid solution, which subsequently destroyed the coordination between ligands and Eu(III). With the pH increasing from 4.0 to 11.5, two new peaks at about 290 and 400 nm appeared on the absorption spectra, owing to the deprotonation of $N_{Pyridyl}$ and the configuration changes of β -diketonate from ketonic type to enol form in the enhanced alkalic environment (Scheme 1). Most notably, deprotonated $N_{Pyridyl}$ and enol form β -diketonate afford stronger affinity for free Eu(III). The absorption at 352 nm partly blue shifted, and the intensity at 290 and 400 nm slightly decreased with the pH value increased from 11.5 to 13.0, all these can be ascribed to the OH^- induced partial disassemble of the Eu(III)- β -diketonate-complex accompanied the formation of the europium-metal hydroxide precipitate.⁴⁵ And the absorption of LOMF-1 was similar with that of LMOF-2 under different pH solution (Fig. S14).

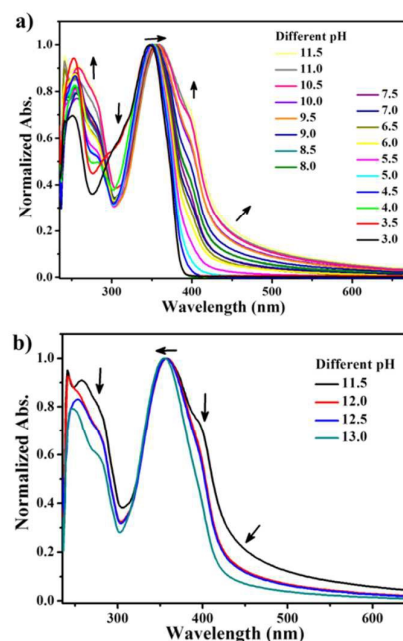


Fig. 3. Normalized absorption spectra of LMOF-2 (10 μ M) under different pH conditions ($H_2O/DMSO$, $v/v=5/1$) (pH: a) 3.0-11.5, b) 11.5-13.0).

Detection pH and acid-base vapors by films

To check if any influence existed from the employed materials, the spectral properties of the free papers and silica plates were investigated before and after testing pH and organic vapors. As shown in Fig. S16a and b, not any luminescence can be observed, demonstrating that both the silica plate and paper matrix can be good film candidates. Then the films containing LMOFs were prepared with uniform luminescence intensity (Fig. S16c).

The luminescence intensity at 612 nm enhanced along with the pH values increased from 4.0 to 13.0 for LMOF-2 loaded papers (Fig. 4), demonstrating its excellent sensitivity to a wider pH range than the above mentioned solution case. What's more, the luminescence performance of the paper was clearly visible by the naked eye under UV light. All these illustrated that the spectroscopic properties of LMOF-2 was improved in strong alkali environment after loaded on the papers, the reason is that the coordination between the ligands and Eu(III) can be destroyed under strong alkali condition and Eu-hydroxide precipitates can be formed in the solution case.⁴⁵ While, all the ligands and Eu(III) were fixed and kept on the paper even though the coordinations were broken up, providing a reversible coordination and decomposition condition along with the pH related acid-base alternation.

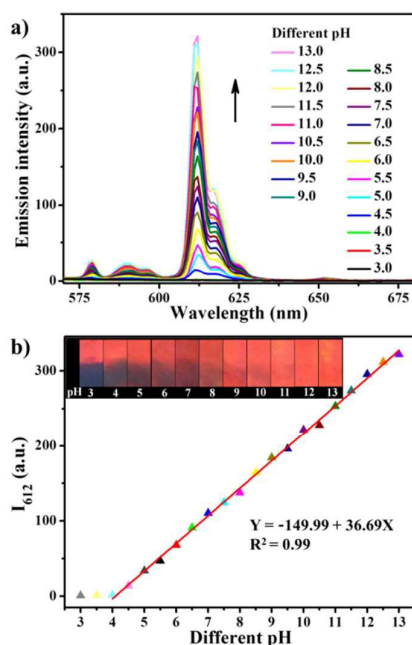


Fig. 4. The luminescence of the LMOF-2 loaded papers under different pH conditions. a) The emission spectra (λ_{ex} =385 nm, slits: 3/3 nm). b) The relationship between the intensity at 612 nm and pH values. Inset: Photos of the papers under UV light (365 nm) after soaked with different pH solution.

As shown in Fig. 5, amine vapors like aqueous ammonia, hydrazinehydrate and ethylenediamine etc. can induce strong luminescence for LMOF-2 loaded paper. While, acid ambiances like methanoic acid, acetic acid and HCl quenched the luminescence to some extent. The luminescence intensity can be easily adjusted by the different pH environment and the process was quite reversible for several times. Especially, the photoluminescence changes of papers were easily visible by the naked eye under UV light (365 nm), which is very helpful for the detection of volatile amines, acidulation and alkalization substances in industrial fields, and soil or water in the environment. Similar results can be observed for the corresponding LMOF-2 loaded silica plate (Fig. S22 and S23), and the same trend can be acquired in the case of LMOF-1 loaded films (Fig. S18 - S21).

Furthermore, the sensing principle of the films was studied. Eu(III) was coordinated with DBM and Phen or BPY to shape LMOFs

and then LMOFs were fixed onto substrates forming strong luminescent films. In acidic environment, the luminescence of the films quenched due to the damage of LMOFs by the protonation of Phen and BPY, as well as the ketonic transformation of DBM.³⁰⁻³⁴ While, in alkalic environment, LMOFs loaded films exhibited strong luminescence owing that alkalic surroundings contribute to the formation of LMOFs. However, under strong base conditions, the luminescence of LMOFs in solution was observed weaker than the corresponding LMOFs loaded films (Fig. S13, S18 and S20), owing that the coordination between the ligands and Eu(III) could be destroyed and some Eu-hydroxide precipitates generated in solution.

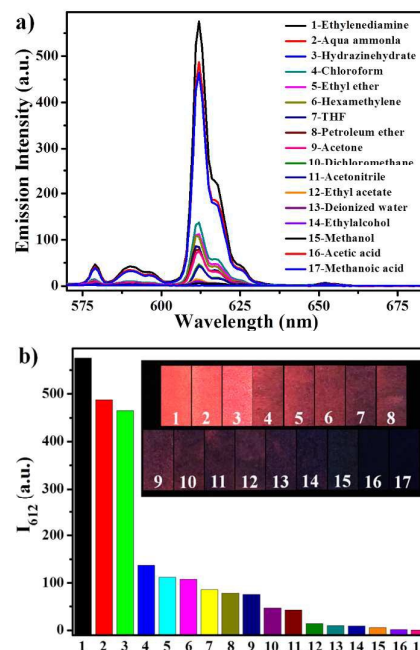


Fig. 5. a) The emission spectra of LMOF-2 loaded papers under different vapors (λ_{ex} =385 nm, slits: 3/5 nm). b) The emitting intensity at 612 nm (serial number corresponding to different vapors in a)). Inset: The digital photos of the tested papers under UV light (365 nm).

Conclusion

In conclusion, a simple strategy to load LMOFs on the filter paper and silica plate was provided, which has the advantages of easy preparation, low cost and excellent performance. Especially, the as-mentioned functional films can be employed for the detection of pH from 4 to 13 as well as volatile amine and acid vapors. All these results can provide theoretical reference and experimental method for pH and vapors/gases detection in the future.

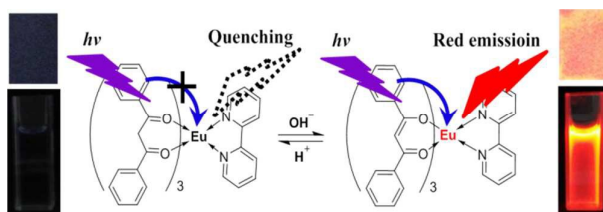
Acknowledgements

This work was financially supported by the Scientific Research Foundation of Northwest A&F University (Z111021103 and Z111021107), the National Natural Science Foundation of China (No. 21272030, 21472016, 21306019, 21576042), State Key Laboratory of Chem/Biosensing and Chemometrics, Hunan University (No. 2013005).

Notes and references

1. R. Wang, X. Y. Dong, H. Xu, R. B. Pei, M. L. Ma, S. Q. Zang, H. W. Hou and T. C. Mak, *Chem. Commun.*, 2014, **50**, 9153-9156.
2. Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2012, **112**, 1126-1162.
3. X. Zhao, S. Li, L. Xu, W. Ma, X. Wu, H. Kuang, L. Wang and C. Xu, *Biosens. Bioelectron.*, 2015, **70**, 372-375.
4. S. V. Eliseeva and J.-C. G. Bünzli, *Chem. Soc. Rev.*, 2010, **39**, 189-227.
5. X. Wang, H. Chang, J. Xie, B. Zhao, B. Liu, S. Xu, W. Pei, N. Ren, L. Huang and W. Huang, *Coordin. Chem. Rev.*, 2014, **273-274**, 201-212.
6. T. D. Ashton, K. A. Jolliffe and F. M. Pfeffer, *Chem. Soc. Rev.*, 2015, **44**, 4547-4595.
7. W. Xu, Y. Zhou, D. Huang, M. Su, K. Wang and M. Hong, *Inorg. Chem.*, 2014, **53**, 6497-6499.
8. L. Su, T. Shu, Z. Wang, J. Cheng, F. Xue, C. Li and X. Zhang, *Biosens. Bioelectron.*, 2013, **44**, 16-20.
9. Y.-H. Chan, J. Chen, Q. Liu, S. E. Wark, D. H. Son and J. D. Batteas, *Anal. Chem.*, 2010, **82**, 3671-3678.
10. R. Ali, T. Lang, S. M. Saleh, R. J. Meier and O. S. Wolfbeis, *Anal. Chem.*, 2011, **83**, 2846-2851.
11. S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee and S. K. Ghosh, *Angew. Chem. Int. Ed.*, 2013, **52**, 2881-2885.
12. Y. Li, Y. Tian, Y. Hua and S. Xu, *J. Non-Cryst. Solids*, 2013, **376**, 38-42.
13. Z. Li, P. Li, Q. Xu and H. Li, *Chem. Commun.*, 2015, **51**, 10644-10647.
14. L. Yan, Y. N. Chang, W. Yin, X. Liu, D. Xiao, G. Xing, L. Zhao, Z. Gu and Y. Zhao, *Phys. Chem. Chem. Phys.*, 2014, **16**, 1576-1582.
15. J. Chen, F. Y. Yi, H. Yu, S. Jiao, G. Pang and Z. M. Sun, *Chem. Commun.*, 2014, **50**, 10506-10509.
16. X. Shen and B. Yan, *J. Mater. Chem. C*, 2015, **3**, 7038-7044.
17. P. Li, Y. Zhang, Y. Wang, Y. Wang and H. Li, *Chem. Commun.*, 2014, **50**, 13680-13682.
18. M. K. Tsang, G. Bai and J. Hao, *Chem. Soc. Rev.*, 2015, **44**, 1585-1607.
19. S. Li, L. Xu, W. Ma, X. Wu, M. Sun, H. Kuang, L. Wang, N. A. Kotov and C. Xu, *J. Am. Chem. Soc.*, 2016, **138**, 306-312.
20. Y. Zhu, Y. Cai, L. Xu, L. Zheng, L. Wang, B. Qi and C. Xu, *ACS Appl. Mater. Inter.*, 2015, **7**, 7492-7496.
21. W. Guan, W. Zhou, J. Lu and C. Lu, *Chem. Soc. Rev.*, 2015, **44**, 6981-7009.
22. E. Moretti, L. Bellotto, M. Basile, C. Malba, F. Enrichi, A. Benedetti and S. Polizzi, *Mater. Chem. Phys.*, 2013, **142**, 445-452.
23. E. Moretti, A. Talon, L. Storaro, A. Le Donne, S. Binetti, A. Benedetti and S. Polizzi, *J. Lumin.*, 2014, **146**, 178-185.
24. R. J. Meier, S. Schreml, X. D. Wang, M. Landthaler, P. Babilas and O. S. Wolfbeis, *Angew. Chem. Int. Ed.*, 2011, **50**, 10893-10896.
25. Y. Zhang, L. Gao, L. Wen, L. Heng and Y. Song, *Phys. Chem. Chem. Phys.*, 2013, **15**, 11943-11949.
26. Y. Li, X. Wang and J. Sun, *Chem. Soc. Rev.*, 2012, **41**, 5998-6009.
27. O. Shekhah, J. Liu, R. A. Fischer and C. Woll, *Chem. Soc. Rev.*, 2011, **40**, 1081-1106.
28. L. V. Meyer, F. Schonfeld and K. Muller-Buschbaum, *Chem. Commun.*, 2014, **50**, 8093-8108.
29. B. Angélique and R. A. Fischer, *Chem. Rev.*, 2012, **112**, 1055-1083.
30. V. Pramod Kumar, K. Federico, S. Andreas, N. Patrick and B. Tobias, *J. Am. Chem. Soc.*, 2014, **136**, 14981-14989.
31. H. Doe, K. Yoshioka and T. Kitagawa, *J. Electroanal. Chem.*, 1992, **324**, 69-78.
32. Z. Yoshida and H. Freiser, *J. Electroanal. Chem.*, 1984, **162**, 307-319.
33. K. Dimitrou, A. D. Brown, K. Folting and G. Christou, *Inorg. Chem.*, 1999, **38**, 1834-1841.
34. A. Samotus, A. Kanas, W. Glug, J. Szklarzewicz and J. Burgess, *Transit. Metal Chem.*, 1991, **16**, 614-617.
35. Y. A. Ustynyuk, N. E. Borisova, V. A. Babain, I. P. Gloriozov, A. Y. Manuilov, S. N. Kalmykov, M. Y. Alyapyshev, L. I. Tkachenko, E. V. Kenf and N. A. Ustynyuk, *Chem. Commun.*, 2015, **51**, 7466-7469.
36. M. Y. Alyapyshev, V. A. Babain, L. I. Tkachenko, A. Paulenova, A. A. Popova and N. E. Borisova, *Solvent Extr. Ion Exc.*, 2014, **32**, 138-152.
37. F. W. Lewis, L. M. Harwood, M. J. Hudson, A. Geist, V. N. Kozhevnikov, P. Distler and J. John, *Chem. Sci.*, 2015, **6**, 4812-4821.
38. P. K. Shahi, A. K. Singh, S. B. Rai and B. Ullrich, *Sens. Actuat. A-Phys.*, 2015, **222**, 255-261.
39. K. Binnemans, *Chem. Rev.*, 2009, **109**, 4283-4374.
40. L. Melby, N. Rose, E. Abramson and J. Caris, *J. Am. Chem. Soc.*, 1964, **86**, 5117-5125.
41. H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512-7515.
42. D. A. Thornton, *Coordin. Chem. Rev.*, 1990, **104**, 173-249.
43. K. Nakamoto, 2009.
44. C. Malba, U. P. Sudhakaran, S. Borsacchi, M. Geppi, F. Enrichi, M. M. Natile, L. Armelao, T. Finotto, R. Marin, P. Riello and A. Benedetti, *Dalton T.*, 2014, **43**, 16183-16196.
45. P. Chen, Q. Li, S. Grindy and N. Holten-Andersen, *J. Am. Chem. Soc.*, 2015, **137**, 11590-11593.

For TOC



A simple luminescence sensing strategy has been designed for pH and amine vapors detection after loaded luminescent compound $\text{Eu}(\text{DBM})_3\text{Phen}$ (LMOF-1), $\text{Eu}(\text{DBM})_3\text{BPY}$ (LMOF-2) on portable matrices such as neutral silica plate and normal filter paper. The easy-prepared films not only displayed response over a pH range of 4-13 but also can be employed to sense volatile amines or acids vapors like ammonia, ethylenediamine, acetic acid and hydrochloric acid etc., which is significant for portable pH or acid-base vapors detection.