

# ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

# A Luminescent Europium (III)- $\beta$ -diketonate complex Hosted in Nanozeolite L as a Turn-On Sensor for Basic Molecules

Peng Li<sup>a</sup>, Yuzhao Zhang<sup>b</sup>, Yige Wang<sup>a</sup>, Yanji Wang<sup>a</sup> and Huanrong Li<sup>a\*</sup>

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

The luminescence efficiency of  $\text{Eu}^{3+}$ - $\beta$ -diketonate complexes entrapped within the channels of nanozeolite L is severely decreased by the acid environment in the channels. The neutralization of the acid sites can remarkably increase the luminescent efficiency due to the formation of complexes with high coordination number. Herein we report a simple, effective and robust luminescent sensor for basic molecules (such as amines) based on the above observations.

Detection of toxic gases and vapors of volatile organic compounds (VOCs) is attracting increasing attention because of the variety of applications that can be found in many different fields.<sup>1</sup> Luminescent microporous MOFs used for this purpose has received considerable attention due to the integrity of luminescence and accessible porosity within such materials which makes them promising candidates for chemical sensing applications.<sup>2</sup> Lanthanide MOFs are especially attractive for this purpose because they have sharp and characteristic emissions and long-lived excited state lifetime of trivalent lanthanide ions.<sup>2c, 3</sup> As an analogy of luminescent MOFs, host-guest materials of encapsulating lanthanide complexes within microporous zeolite possess similar properties with some LnMOFs, such as crystalline frameworks, permanent porosities and collaborative luminescence properties.<sup>4</sup> However, the use of  $\text{Ln}^{3+}$  complexes hosted in zeolite to vapor detection has been rarely reported although conventional microporous zeolites have been fully exploited in the application field of gas sensing.<sup>5</sup>

Zeolite L (ZL) is a crystalline aluminosilicate consisting of strictly one dimensional channel. The channels have a smallest diameter of about 0.71nm, and the largest internal diameter is about 1.26 nm. Suitable guests including luminescent lanthanide complexes can be incorporated within the channels (Fig. 1a).<sup>4c, 6</sup> We have observed obviously improved photo-stability of  $\text{Eu}^{3+}$ - $\beta$ -diketonate complexes after encapsulation within the channels of ZL<sup>7</sup>, silica shell was coated on the hybrid naocomposites to seal the channel entrances. Non-luminescent terbium (III) complexes was then grafted to the silica shell to detect dipicolinic acid,  $\text{Eu}^{3+}$ - $\beta$ -diketonate complexes inside the channels was well protected by the silica shell and was used as an internal calibration.<sup>5d</sup> Recently, we observed strong acidity inside the channels of  $\text{Eu}^{3+}$ -exchanged ZL and its negative influence on the luminescence yielded of the encapsulated  $\text{Eu}^{3+}$ - $\beta$ -diketonate complexes (Fig. 1a).<sup>5e</sup> Decreasing the proton strength by treating the nanocomposites with ammonia<sup>5e</sup> or silane-containing imidazolium salt<sup>8</sup> can increase the luminescence efficiency through the formation of complexes with high coordination numbers. Inspired by the above observations, herein we report a simple and robust platform for detecting basic molecule vapors based on the encapsulation of  $\text{Eu}^{3+}$ - $\beta$ -diketonate complex within

a nanozeolite L framework (abbreviated as  $(\text{Eu}^{3+}(\text{TTA})_n\text{-NZL}$ , Fig. 1).

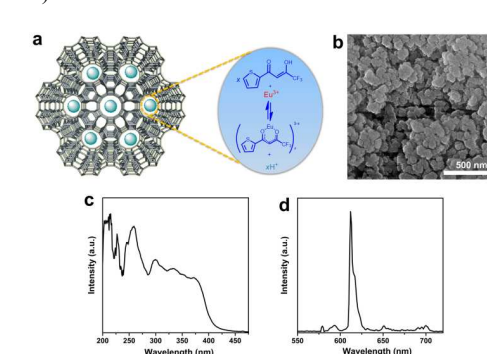
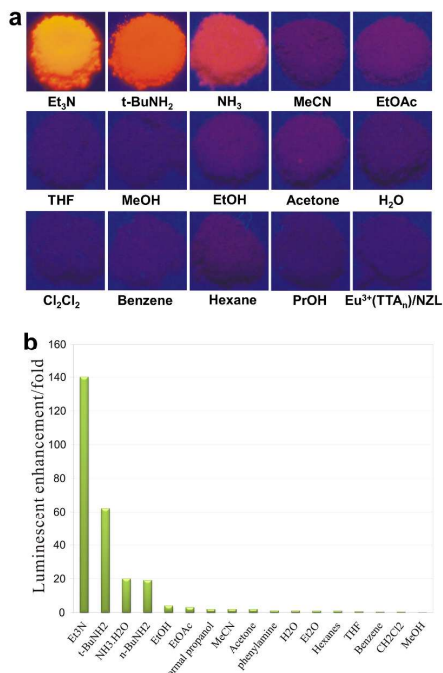


Fig.1 (a) Zeolite L framework projected along c axis with  $\text{Eu}^{3+}(\text{TTA})_n$  loaded in the channels where shows the presence of protons. (b) SEM image of  $\text{Eu}^{3+}(\text{TTA})_n\text{-NZL}$ . Excitation spectra at 612nm (c) and emission spectra excited at 345nm (d) of  $\text{Eu}^{3+}(\text{TTA})_n\text{-NZL}$ .

The  $\text{Eu}^{3+}(\text{TTA})_n\text{-NZL}$  nanocomposite was easily prepared on a large scale and the film of which can be simply realized by casting an aqueous suspension of  $\text{Eu}^{3+}(\text{TTA})_n\text{-NZL}$  on various substrates.<sup>7-8</sup> The  $\text{Eu}^{3+}$  and TTA loading can be experimentally determined to roughly be 0.66/u.c. and 3/u.c., respectively. This means the content of  $\text{Eu}^{3+}$  ions in the sample is less than 5%. FT-IR spectrum (ESI, Fig. S1†) shows a very intense anti-symmetric  $\text{V}_{\text{as}}(\text{T-O})$  stretching vibration ( $\text{T}=\text{Si}^{4+}$  or  $\text{Al}^{3+}$ ) around  $1100\text{ cm}^{-1}$ . The band at  $1541\text{ cm}^{-1}$  is ascribed to the C=C stretching vibrations of TTA ligand, the absorption band near  $1630\text{ cm}^{-1}$  can be considered as a superposition of the bending vibrations of lattice water molecules (and surface silanol groups) and the C=O stretching vibrations of TTA. The luminescence data of  $\text{Eu}^{3+}(\text{TTA})_n\text{-NZL}$  were investigated and shown in Fig. 1c and 1d. The emission spectrum displays characteristic  $\text{Eu}^{3+}$  emissions at 579, 593, 612, 650 and 698 nm attributed to  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$  transition ( $J=0-4$ ) upon excitation with a wavelength of 350 nm. The weakness of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition at 593nm and the higher intensity of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition at 612nm observed in Fig. 1d indicate that the  $\text{Eu}^{3+}$  local environment has low symmetry without an inversion centre.<sup>9</sup> A broad band ranging from 200 to 500 nm is observed in the excitation spectrum, resulting from the absorption of TTA ligand.<sup>5d</sup> The decay time of  $\text{Eu}^{3+}$  is determined to be  $\sim 0.09\text{ ms}$  from the decay curve which is bi-exponential function (ESI, Fig. S1†). However, the luminescence is somehow weak under UV irradiation (Fig. 2a) and the absolute quantum yield is quite low (1.2%). Contact  $\text{Eu}^{3+}(\text{TTA})_n\text{-NZL}$  with  $\text{NH}_3\cdot\text{H}_2\text{O}$  vapor can obviously enhance its luminescence ( Fig.

2a)<sup>5e, 7</sup>. This finding promoted us to examine the sensing ability of  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$  for small molecules.



5 Fig. 2 (a) Digital photos of  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$  upon contact with various vapors for 1h taken and near UV illumination. (b) Increase in emission intensity of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition at 612 nm in exposure to vapors of various solvents.

The luminescence response of  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$  upon exposure to vapors of various small molecules for 1h were measured and the results are shown in Fig. 2. The boosting of luminescence of  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$  is easily visible by the naked eyes upon near UV excitation (Fig. 2a). We can observe a remarkable enhancement of luminescence intensity by a factor of 15 140, 65, 22 and 20 for vapors of triethylamine ( $\text{Et}_3\text{N}$ ), tert-butylamine ( $t\text{-BuNH}_2$ ), n-butylamine ( $n\text{-BuNH}_2$ ) and  $\text{NH}_3$ , respectively, whereas only about twofold enhancement luminescence can be observed for EtOH, EtOAc, PrOH and acetone (Fig. 2b). Interestingly, it seems that vapors with certain features such as basicity tend to boost the luminescence of the nanocomposite significantly. This means that our nanocomposite show high capacity to discriminate basic molecules (e.g.,  $\text{Et}_3\text{N}$ ) among others. To understand the ability of distinguishing basic molecules from non basic ones, one should have detailed knowledge of the environment inside the channels of  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$ . Actually, a strong proton activity can be observed inside the channels which results from dissociation of the adsorbed water<sup>5e, 10</sup>. The TTA ligand can be protonated under the acidic environment of hydrated ZL, its protonation competes with full coordination to  $\text{Eu}^{3+}$  and that incomplete coordination is detrimental to the luminescence yield, which can explain why the luminescence efficiency of  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$  is quite low. The luminescence enhancement upon exposure to ammonia gas<sup>5e</sup> or upon modification with a silane-containing imidazolium salt<sup>8</sup> has already been reported by us previously. This means the basic vapor such as some of the amines can decrease the proton strength inside the channels through neutralization and hence favor the formation of  $\text{Eu}^{3+}$   $\beta$ -diketonate complexes of high coordination number. The decrease of proton strength can be obviously probed by the method described elsewhere.<sup>5e, 10</sup> A thionine was used as the probe molecule and it has been reported

that the thionine-encapsulated H-form ZL displays a new band peaking at  $\sim 675$  nm owing to the presence of the doubly protonated thionine.<sup>10</sup> The absorption spectra (ESI, Fig. S3†) reveals that the band at  $\sim 675$  nm disappears upon contact with  $\text{Et}_3\text{N}$  vapor, indicating the neutralization of acid sites by  $\text{Et}_3\text{N}$  molecules. Furthermore, we observe that the order of luminescence boosting for the selected amines is  $\text{Et}_3\text{N} > t\text{-BuNH}_2 > n\text{-BuNH}_2 > \text{NH}_3$ . This order is fully in accordance with the trend of the pKa of the corresponding conjugate acid. Notably, no obvious luminescence boosting can be observed for aniline due to its much weaker basicity with respect to the aliphatic amine such as  $\text{Et}_3\text{N}$ , implying the enhancement in luminescence performances is predominantly controlled by the base strength of the small molecules.

Table 1. Photophysical data.

sample	$\tau$ [ms]	$Q$ [%]	$I({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)/I({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$
$\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$	0.09	1.2	13.2
$\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL@Et}_3\text{N}$	0.71	18	14.9
$\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL@t-BuNH}_2$	0.53	11	14.1
$\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL@n-BuNH}_2$	0.40	8.0	14.0
$\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL@NH}_3$	0.36	6.2	14.0

The interpretation is also supported by the behaviour of the intensity ratio  $I({}^5\text{D}_0 \rightarrow {}^7\text{F}_2)/I({}^5\text{D}_0 \rightarrow {}^7\text{F}_1)$  and the luminescence decay. It reveals that the ratio increases from 13.2 to 14.9, 14.1, 14.0 and 14.0 after exposure to the vapor of  $\text{Et}_3\text{N}$ ,  $t\text{-BuNH}_2$ ,  $n\text{-BuNH}_2$  and  $\text{NH}_3$ , respectively. The intensity ratio has frequently been used as a measure for the asymmetry of  $\text{Eu}^{3+}$  site, which can become larger with increasing interaction of  $\text{Eu}^{3+}$  with its neighbours due to the decrease of the site symmetry.<sup>9</sup> Therefore, the increased intensity upon contact with the basic vapor reflects the decreased symmetry of  $\text{Eu}^{3+}$  site and the larger  $\text{Eu}^{3+}$ -ligand, implying a more complete coordination to the  $\beta$ -diketonate. The luminescence decays (ESI, Fig. S3†) are well represented by bi-exponential, the average decay time also increases remarkably as shown in Table 1. The prolonged lifetime of  $\text{Eu}^{3+}$  excited state after exposure to the basic vapors is ascribed to the displacement of water molecules and / or OH groups from the first coordination sphere via the coordination to TTA ligands. Interestingly, the absolute quantum yield determined from the integrating sphere of  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$  is also increased by exposure to vapors (Table 1). The order of increase in quantum yield is in good agreement with that of the luminescent intensity and of lifetime.

Fast response is an important parameter for a desired sensor. We therefore test the response rate of  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$  using triethylamine as the model analyst. The emission spectra of layers on glass substrate were measured, before and after exposing them to the equilibrated vapor of  $\text{Et}_3\text{N}$  for varied periods of time. As shown in Fig. S4 in ESI†,  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$  shows a very rapid and evident response to the tested chemical. Within 20 seconds, the luminescence boosting reaches almost the maximum.

Interestingly, when the used samples of  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$  was exposed to a formic acid (FA)-gas riched environment for several seconds, the red luminescence disappeared to the naked eyes, subsequent exposure to  $\text{Et}_3\text{N}$  vapor for 5 seconds, the red luminescence was seen by naked eyes (Fig. 3a). The on/off switching can also be reflected from the emission spectra shown

in Fig. 3b. The emission spectra of the film of  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$  were recorded upon alternative exposure to FA gas and  $\text{Et}_3\text{N}$  over several cycles in order to examine the reversibility, the results are shown in Fig. 3c. It reveals  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$  on substrate shows good reversibility at least 6 cycles. Amazingly, the luminescence boosting after the first FA- $\text{Et}_3\text{N}$  cycle is significantly enhanced although the used  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$  could not be completely regenerated and the trend is continued till the fourth cycles (Fig. 3c). The reason for the enhanced luminescence boosting is unknown yet. In addition to the simple synthesis process, the high selectivity towards basic molecules and the fast response as well as good reversibility, the outstanding robustness is another merit of our method. XRD patterns and SEM images (ESI, Fig. S5†) demonstrate that no significant changes in its framework and morphology can be observed.

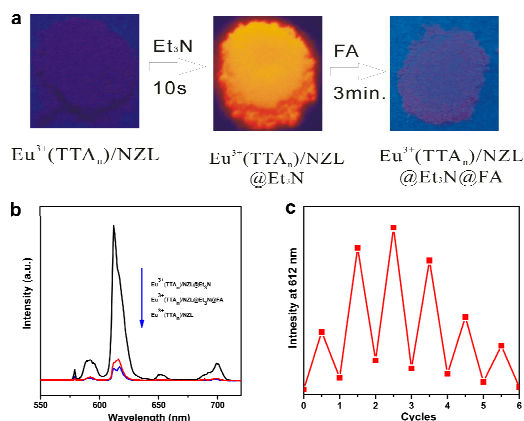


Fig. 3. Acid-base vapor-induced luminescence switching of  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$ . (a) Digital photos of  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$  during the exposure to  $\text{Et}_3\text{N}$ -FA vapor; (b) spectral changes before and after exposure to  $\text{Et}_3\text{N}$ -FA vapor in emission spectra of  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$ ; (c) Responses of emission intensity at 612 nm of  $\text{Eu}^{3+}(\text{TTA}_n)\text{-NZL}$  during the  $\text{Et}_3\text{N}$ -FA vapor exposure cycles.

In summary, we have designed a simple and robust platform for detecting basic molecule vapors based on the encapsulation of  $\text{Eu}^{3+}$ - $\beta$ -diketonate complex within a nanozeolite L framework. The nanocomposite shows a condition selective luminescence turn-on response to basic molecule vapors, a remarkable enhancement in luminescence intensity, lifetime of  $\text{Eu}^{3+}$  ions and the absolute quantum yield are observed. The stationary and time resolved spectroscopy studies suggest that the mechanism responsible for the turn-on response to basic molecule vapors is that basic molecules is favorable to the formation of  $\text{Eu}^{3+}$ - $\beta$ -diketonate complexes of high coordination numbers through decreasing the proton strength of the channels. The turn-on luminescence response can be switched-off by acid vapors. Our approach has various desirable properties, such as easy and scalable synthesis, cost-effective, fast response rates and good reversibility.

Financial support by the National Key Basic Research Program (2012CB626804), the National Natural Science Foundation of China (20901022, 21171046, 21271060, and 21236001), the Tianjin Natural Science Foundation (13JCYBJC18400), the Natural Science Foundation of Hebei Province (No.B2013202243), and Educational Committee of Hebei Province (2011141, LJRC021) is gratefully acknowledged.

## Notes and references

- <sup>a</sup> School of Chemical Engineering and Technology, Hebei University of Technology, Guang Rong Dao 8, Hongqiao Distric, Tianjin 300130 (China). E-Mail: lihuanrong@hebutu.edu.cn
- <sup>b</sup> School of Control Science and Engineering, Hebei University of Technology, Guang Rong Dao 8, Hongqiao Distric, Tianjin 300130 (China)
- † Electronic Supplementary Information (ESI) available: [Experimental and the spectra]. See DOI: 10.1039/b000000x/
- ‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
- 1(a) F. Rock, N. Barsan and U. Weimar, *Chem.Rev.*, 2008, **108**, 705; (b) J. W. Grate, *Chem.Rev.*, 2008, **108**, 726.
- 2(a) Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem.Rev.*, 2012, **112**, 1126; (b) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105; (c) L. V. Meyer, F. Schonfeld and K. Muller-Buschbaum, *Chemical Communications*, 2014, **50**, 8093.
- 3(a) S. Dang, E. Ma, Z.-M. Sun and H. Zhang, *Journal of Materials Chemistry*, 2012, **22**, 16920; (b) B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian and E. B. Lobkovsky, *Advanced Materials*, 2007, **19**, 1693; (c) Y. Cui, B. Chen and G. Qian, *Coordination Chemistry Reviews*, 2014, **273–274**, 76; (d) Y. Li, S. Zhang and D. Song, *Angew. Chem. Int. Ed.*, 2013, **52**, 710.
- 4(a) L. K. D. Sendor, *Adv. Mater.*, 2002, **14**, 1570; (b) H. Maas, A. Currao and G. Calzaferri, *Angew. Chem. Int. Ed.*, 2002, **41**, 2495; (c) P. Cao, Y. Wang, H. Li and X. Yu, *Journal of Materials Chemistry*, 2011, **21**, 2709; (d) Y. Wang, H. Li, L. Gu, Q. Gan, Y. Li and G. Calzaferri, *Microporous and Mesoporous Materials*, 2009, **121**, 1; (e) Y. Wada, M. Sato and Y. Tsukahara, *Angew. Chem. Int. Ed.*, 2006, **45**, 1925; (f) A. Mech, A. Monguzzi, F. Meinardi, J. Mezyk, G. Macchi and R. Tubino, *J. Am. Chem. Soc.*, 2010, **132**, 4574.
- 5(a) Y. Zheng, X. Li and P. K. Dutta, *Sensors*, 2012, **12**, 5170; (b) A. Saha, Z. Panos, T. Hanna, K. Huang, M. Hernández-Rivera and A. A. Marti, *Angewandte Chemie International Edition*, 2013, **52**, 12615; (c) P. Payra and P. K. Dutta, *Microporous and Mesoporous Materials*, 2003, **64**, 109; (d) H. Li, W. Cheng, Y. Wang, B. Liu, W. Zhang and H. Zhang, *Chem. Eur. J.*, 2010, **16**, 2125; (e) T. Wen, W. Zhang, X. Hu, L. He and H. Li, *Chempluschem*, 2013, **78**, 438.
- 6 G. Calzaferri, S. Huber, H. Maas and C. Minkowski, *Angew. Chem. Int. Ed.*, 2003, **42**, 3732.
- 7 Y. Ding, Y. Wang, H. Li, Z. Duan, H. Zhang and Y. Zheng, *J. Mater. Chem.*, 2011, **21**, 14755.
- 8 P. Li, Y. Wang, H. Li and G. Calzaferri, *Angew. Chem. Int. Ed.*, 2014, **53**, 2904.
- 9 K. D. Kyra Lunstroot, Peter Nockemann, Christiane Goerller-Walrand, and S. v. B. Koen Binnemans, Jean Le Bideau, Andre' Vioux, *Chem. Mater.*, 2006, **18**, 5711.
- 10 R. Q. Albuquerque and G. Calzaferri, *Chem. Eur. J.*, 2007, **13**, 8939.
- 11 S. Tang, A. Babai and A.-V. Mudring, *Angew. Chem. Int. Ed.*, 2008, **47**, 7631.