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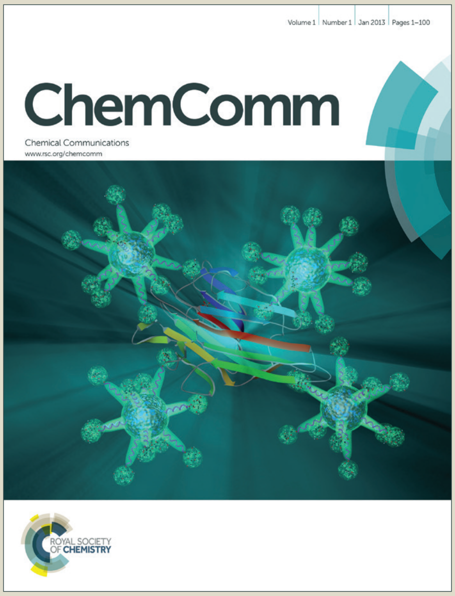

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A ratiometric fluorescent pH sensor based on nanoscale metal-organic frameworks (MOFs) modified by europium (Ⅲ) complex

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We report a new ratiometric fluorescent pH sensor based on nanoscale postsynthetic modified MOF-253. Two types of Eu^{3+} with different characteristic excitation wavelength are realized in MOF-253 by postsynthetic method (PSM). The pH sensor requires no calibration because only one of the two types of Eu^{3+} is affected by the pH variation.

Metal-organic frameworks (MOFs) have received enormous attention in the last two decades.[1] The research of luminescent properties of MOFs is a domain that has only recently been initiated but which is crucial role for luminescent sensors or probes.[2] The luminescent properties of MOFs are very sensitive to their structural characteristics, coordination environment, pore surfaces and their interactions with guest species. This endows MOFs to inherent advantage in luminescent sensing, especially for the lanthanide-based MOFs.[3] When these materials are scaled down to the nano-regime to afford nanoscale metal-organic frameworks (nMOFs), they have been explored in the biomedical applications.[4]

One of the main concerns in luminescent sensing is to detect the pH of aqueous solution, especially for monitoring small pH change in biological environments and living cell.[5] Only three pH-MOF sensors have been reported: two of them realize the sensing pH by Zr-base MOF (PCN-225 and UiO-66-NH_2) and fluorescent pH-dependent ligand, and the other one is a Eu^{3+} pH-MOF based on π–π stacking.[6] But some flaws is still existed: the pH-MOFs based on Zr^{4+} and pH-dependent ligand have not linear relationship between pH value and fluorescent intensity; the stability of the MOFs based on π–π stacking is not excellent because π–π stacking is weak interaction. Meantime, this field also leaves much to be desired: the nanoscale size is important for assembling device and biological applications;[7] the sensitivity and accuracy could be effectively improved by utilizing a ratiometric pattern because a dual emission system can effectively minimize measurement errors.[8]

Actually, the self-assembly of Eu^{3+} ion with β-diketonate or Lewis bases is driven by pH of aqueous solution.[9] Moreover, the self-assembly driven by pH could significant impact on the Eu^{3+} characteristic luminescence.[10] Recently, we have reported the assembling lanthanide complex with β-diketonate to MOF-253 through postsynthetic method (PSM).[11] Moreover, we also reported nanoscale MOF-253 could be applied in intracellular sensing.[12] So, this intrigues our interest in combining the self-assembly driven by pH and the inherent advantage of MOFs (porous structure and adsorption capacity for small molecule) to build a nanoscale pH-dependent fluorescent MOFs. Herein, we reported a new ratiometric pH sensor based on nanoscale postsynthetic modified MOF-253. By PSM, two types of Eu^{3+} with different characteristic excitation wavelength are realized in MOF-253 simultaneously (Figure 1), and then one of them is insensitive to pH, another one is sensitive to pH.

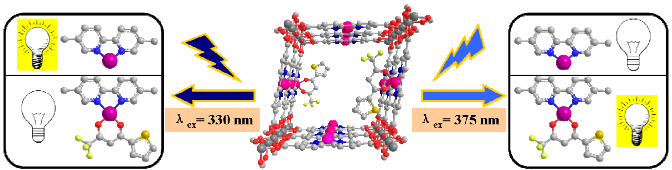

Figure 1. Schematic diagram of MOF-253 modified by Eu^{3+} complex with TTA, there are two types of Eu^{3+} with different ligand in the modified MOF-253 (Eu1 and Eu2), Eu1 could emit Eu^{3+} characteristic light under the excitation at 330 nm and Eu2 could emit Eu^{3+} characteristic light under the excitation at 375 nm.

MOF-253 is an ideal platform to carry lanthanide complex because that bipyridine in the ligend could fix and sensitize lanthanide ion simultaneously.[11] The representative structure of MOF-253 has been isolated by PXRD and a Pawley refinement in the reported work.[13] MOF-253-Eu-TTA is prepared through PSM, which Eu^{3+} ion is introduced to MOF-253 firstly (record as MOF-253-Eu), the deprotonated TTA (TTA = 2-thenoyltrifluoroacetone) is used to further sensitize Eu^{3+} ion (The details see ESI). Bipyridine is a neutral molecule, so NO^{3-} in the MOFs is used as counter ion.[14] The deprotonated TTA could construct a six-member chelate ring with Eu^{3+} ion.[15] In PSM, the amount of Eu^{3+} ion is 4 times of TTA (according to feed ratio) for building two different coordination environments of Eu^{3+} ion, one of them is only linked by bipyridine, named as Eu1, the other one has two ligand (bipyridine and TTA),

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named as Eu2. The molar ratio of Al^{3+}/Eu^{3+} ion in MOF-253-Eu is checked by inductively coupled plasma (ICP) analysis.

As-synthesized materials based on MOF-253 are confirmed by PXRD (Figure S1), nitrogen adsorption/desorption isotherms (Figure S2) and FT-IR spectroscopy (Figure S3). The size of MOF-253-Eu-TTA is almost less than 100 nm according to the image of transmission electron microscopy (TEM) and scanning electron microscope (SEM) (Figure S4). After introducing Eu^{3+} ion or TTA, the crystallization degree of MOF-253-based hybrid material is slightly weakened, but the framework is still integrated from PXRD (Figure S1) and FT-IR spectroscopy (Figure S3). Meantime, the characteristic absorbance of NO_3^- (1377 cm^{-1}) observed in the FT-IR spectroscopy of MOF-253-Eu and MOF-253-Eu-TTA explains the existence of NO^{3-}; the absorbance at 1717 cm^{-1} in MOF-253-Eu-TTA is ascribed to the absorption of C=O of TTA.

The emission of MOF-253-Eu exhibit the Eu^{3+} characteristic transitions at 579, 593, 614, 648 and 687 nm under the excitation at 330 nm, which are ascribed to the $^5D_0\rightarrow{}^7F_J$ (J = 0-4) transitions (Figure S5). The excitation spectrum of MOF-253-Eu is obtained by monitoring the emission wavelength at 614 nm, which is dominated by a broad band centered at about 330 nm and two sharp lines, assigned to the $^7F_0\rightarrow{}^5D_2$ (at 463 nm) and $^7F_0\rightarrow{}^5L_6$ (at 394 nm). The intensity ration of $^5D_0\rightarrow{}^7F_2$ to $^5D_0\rightarrow{}^7F_1$ is 7.0.

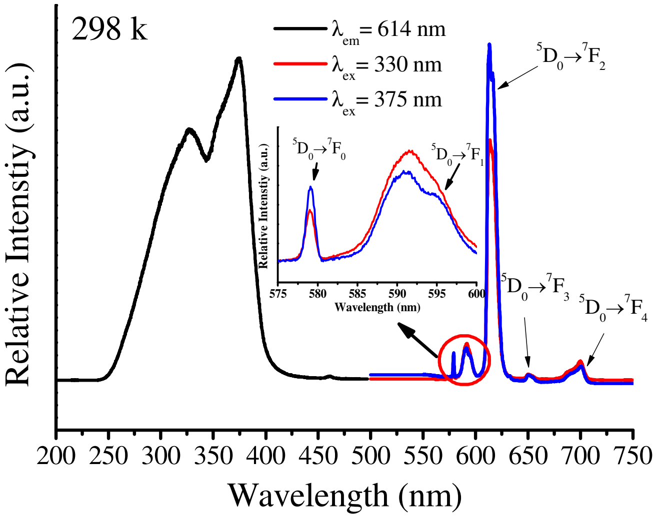

Figure 2. The excitation spectrum (λ_{em} = 614 nm) of MOF-253-Eu-TTA (black) and the emission spectra of MOF-253-Eu-TTA, λ_{ex} = 330 nm (red) and λ_{ex} = 375 nm (blue), which is record under 298 k.

Generally, the excitation wavelength of trivalent lanthanide ion greatly depends on the ligands, which is so call "antenna effect".[16] The excitation spectrum (298 k) of MOF-253-Eu-TTA is obtained by monitoring the emission at 614 nm, which is dominated by two broad bands centered at about 330 nm and 375 nm (Figure 2). In comparison with the excitation spectrum of MOF-253-Eu (Figure S5), the broad band at 330 nm could be chiefly assigned to excitation of Eu1. And then, the broad band at 375 nm should mostly belong to the excitation of Eu2 for the energy absorb of TTA. Although the emission spectra (298 k) all display the Eu^{3+} characteristic emission and their wavelength of transition $^5D_0\rightarrow{}^7F_J$ (J = 0-4) is basically same (which are obtained by excitation at 330 nm and 375 nm), some tiny difference could still be indicated, such as the different intensity ration of $^5D_0\rightarrow{}^7F_2$ to $^5D_0\rightarrow{}^7F_1$, the intensity ration of $^5D_0\rightarrow{}^7F_2$ to $^5D_0\rightarrow{}^7F_1$ for Eu1 is 7.1 (λ_{ex} = 330 nm) and that for Eu2 is 10.3 (λ_{ex} = 375 nm). According to Judd-Ofelt theory, the intensity ration of $^5D_0\rightarrow{}^7F_2$ to $^5D_0\rightarrow{}^7F_1$ depend on symmetry of Eu^{3+} ion.[17] The intensity ration of $^5D_0\rightarrow{}^7F_2$ to $^5D_0\rightarrow{}^7F_1$ for Eu1 is similar to that for MOF-253-Eu. This proves the broad band at 330 nm is chiefly assigned to excitation of Eu1 again. Due to the energy transfer from TTA, the lifetime (298 k) of Eu2 (λ_{ex} = 375 nm) is 422.60 μs, which is obviously shorter than the lifetime of Eu1, 517.99 μs (λ_{ex} = 375 nm) (Figure S6). The quantum yields of MOF-253-Eu-TTA are about 15% (λ_{ex} = 330 nm) and 18% (λ_{ex} = 375 nm).

Under 77 K, the intensity of the board band at 375 nm (Eu2) in the excitation spectrum is obviously enhanced (Figure S7). This is because that the rigid framework of bipyridine could effectively reduce the effect from thermovibration of molecule.[15] For the luminescence from framework (Figure S8), the basic line of the emission line obtained under excitation at 375 nm is slightly higher than that obtained under excitation at 330 nm (Figure S7). The lifetime (77 k) under excitation wavelength at 375 nm is 694.52 μs, increased by 271.92 μs in comparison with the data record under 298 k (Figure S9), meantime, the lifetime under excitation wavelength at 330 nm is only enhanced by 203.16 μs, which is 721.17 μs (77 k). In the view of the overlap of the two board bands in excitation spectra (77 k), the actual increase in lifetime of Eu1 should be much less. Those all prove that the two types of Eu^{3+} with different coordination environment and excitation wavelength are actually existed in the modified MOF-253.

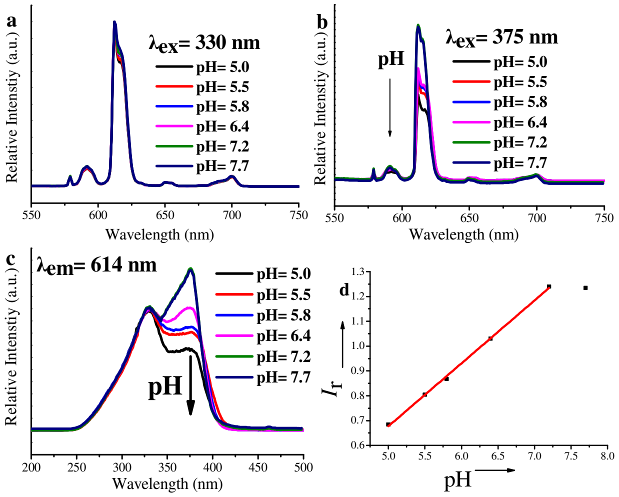

Figure 3. The emission spectra of MOF-253-Eu-TTA in different pH aqueous solution, λ_{ex} = 330 nm for (a) and λ_{ex} = 375 nm for (b); (c) the excitation spectra of MOF-253-Eu-TTA in different pH aqueous solution (λ_{em} = 614 nm); (d) the linear variation of the $^5D_0\rightarrow{}^7F_2$ emission intensity ratio (I_r) of the two Eu^{3+} type with different excitation wavelength, Eu1 (λ_{ex} = 330 nm)/ Eu2 (λ_{ex} = 375 nm).

Our preliminary results on the use of MOF-253-Eu-TTA as a pH sensor are very encouraging. The sensor has a linear response in the pH range 5.0-7.2, which is required for work with biological fluids such as blood and culture cell media. Acid or alkali could react with Al^{3+} ion to ruin the framework because that aluminum is amphoteric metal. At a pH = 4 buffered solution, the sensor is directly dissolved and can not be centrifuged even if under 13000 rpm for 10 min. Meantime, for pH value above 8, europium hydroxide would be formed as a result of the competition for the metal coordination sites between the hydroxide groups and the ligand. Hence, it is different to achieve the accurate pK_a according to the reported measurement.[9c]

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For MOF-253-Eu-TTA, there should be two different pK_a, one for TTA and the other one for bipyridine. The pK_a about deprotonation of the Lewis bases (phenanthroline) ligand is about 3.6, and Eu^{3+} characteristic luminescent intensity is almost unchanged at pH 5-7.[9b] Meantime, the pK_a about deprotonation of the α-proton of TTA is about 5.3 according to the reported work, although different system would have some slightly difference in accurate pK_a.[10b] So, the MOF-253-Eu-TTA requires no calibration because only one of the two types of Eu^{3+} is affected by the pH variation in the range 5 to 7.2. The MOF-253-Eu-TTA structure is stable at pH 5.0-7.7 which is checked by PXRD (Figure S1). The emission intensity of Eu1 (λ_{ex} = 330 nm) remains almost unchanged in different pH solution (Figure 3a). Meanwhile, the emission intensity of Eu2 (λ_{ex} = 375 nm) weakens with the decrease of the value of pH for the protonation of the α-proton of TTA (Figure 3b). The change on emission intensity is correspond to the results of excitation spectra, which obtained by monitoring the emission wavelength at 614 nm (Figure 3c). By following the $^5D_0 \rightarrow {}^7F_2$ emission intensity ratio (I_r) of the two Eu^{3+} type (Eu1/Eu2), the pH of the solution could be determined. In pH range of 5.0-7.2, the relation of $^5D_0 \rightarrow {}^7F_2$ emission intensity ratio (I_r) and the pH value present a good linearity (R = 0.9991) (Figure 3d).

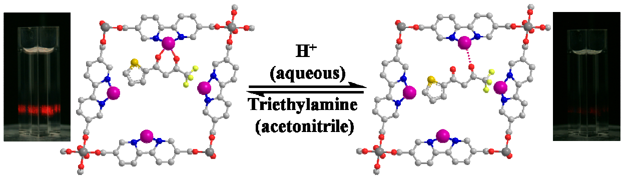

Figure 4. Schematic representation of the pH sensor based on MOF-253, H^+ proton could impair the sensitization of TTA to Eu^{3+} through breaking the six-member chelate ring, and the thriethylamine could recover the sensitization; the insets are the photograph of MOF-253-Eu-TTA in pH = 5 aqueous solution (right) and in pH = 7.2 aqueous solution (lift) (λ_{ex} = 375 nm).

The framework play two irreplaceable role in this system: the first is to realize two types of Eu^{3+}, which have been discussed at above; the second is to hold TTA small molecule in the pore. The pH-sensing mechanism of Eu^{3+} complex with TTA is that the H^+ proton could break the six-member chelate ring (built by TTA and Eu^{3+} ion) to impair the sensitization of β-diketonate to Eu^{3+}, as a result, the Eu^{3+} characteristics luminescence intensity would be quenched instantaneously.[10a] For the single Eu^{3+} complex with TTA, the free TTA would be disappeared into the solution after the broken of six-member chelate ring. However, when the Eu^{3+} complex is assembled into MOFs, some difference is occurred. The free TTA would be still in the pore after the broken of the six-member chelate ring because MOFs have the adsorption capacity to hold those molecules (TTA). As a consequence, the sensitization from TTA is still existence, but the effect is lessened. More importantly, the weakened sensitization could keep the excitation wavelength of Eu2 is still at 375 nm and not changed to 330 nm, even if the six-member chelate ring is broken (Figure 4). This is why the luminescent intensity of Eu1 is not enhanced after the broken of six-member chelate ring, and the luminescent intensity of Eu2 is only weakened, not vanished.

For proving this, a comparison experiment has been made. MOF-253-Eu@TTA is prepared by the same way to MOF-253-Eu-TTA except for no triethylamine added in the process. After adding MOF-253-Eu, the intensity of TTA in UV-Vis spectrum is significantly decreased (Figure S10) (The details of measurement see ESI). This indicates almost of TTA in the solution is absorbed by MOF-253-Eu even if no triethylamine added. Meanwhile, the broad band at 375 nm in excitation spectra of MOF-253-Eu@TTA could prove the existence of sensitization from TTA to Eu^{3+}, but the intensity of the broad band at 375 nm is obviously weaker than the broad band at 330 nm (Figure S11). Comparison with the luminescent spectra of MOF-253-Eu-TTA, the sensitization effect of TTA to Eu^{3+} is obviously enhanced after adding triethylamine to form the six-member chelate ring. The form of six-member chelate ring could also be detected by the change of the intensity ratio of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$, the intensity ration of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ for MOF-253-Eu@TTA (λ_{ex} = 375 nm) is 8.1, and that for MOF-253-Eu-TTA (λ_{ex} = 375 nm) is 10.3. Moreover, the result is correspond to the change trend of the intensity ration of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ for MOF-253-Eu-TTA (λ_{ex} = 375 nm) in different pH aqueous solution, which have been listed in Table S1. This also proves the sensing pH of MOF-253-Eu-TTA is actually due to the protonation of TTA. Moreover, the example about using undeprotonated β-diketonate to sensitize lanthanide ion is numerous in porous materials.[18]

For further proving the free TTA is in the pore, triethylanmine is used to recover the luminescent intensity (λ_{ex} = 375 nm) of MOF-253-Eu-TTA which have been soaked in pH = 5 aqueous solution (Figure 4). (The details of the recover experiment see ESI). The luminescent spectra of MOF-253-Eu-TTA during recover experiment are similar with the original MOF-253-Eu-TTA (Figure S12). The results indicate the self-assembly driven by pH is reversible in the MOFs, which is corresponded to the reported work about the self-assembly of Eu^{3+} ion with β-diketonate.[10] The regeneration is an important topic for luminescent probes because that the regeneration is useful for the research of sensing mechanism.[19] For MOF-253-Eu-TTA, though the recover experiment was a success, we can not ensure the pH sensor based on MOF-253 can be 'switched' on-off over several cycles because that the stability of MOFs is not very outstanding in the inorganic materials and the framework of MOFs maybe degraded after too many cycles. But this would not be affect the application of MOF-253-Eu-TTA in pH sensing because that most of luminescent sensor is irreversible, especially for those used in biomedicine.[20]

In conclusion, we present a new ratiometric pH sensor based on nanoscale postsynthetic modified MOF-253. The sensor does not require external calibration for the pH range 5.0-7.2, which is the common range for the study of biological fluids. We hope this work could open new possibilities for the use of designing luminescent hybrid biomaterial in biomedical applications.

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Notes and references

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† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/

1 (*a*) H. C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673; (*b*) J. R. Li, J. Sculley and H. C. Zhou, *Chem. Rev.*, 2012, **112**, 869; (*c*) A. U. Czaja, N. Trukhan and U. Muller, *Chem. Soc. Rev.*, 2009, **38**, 1284; (*d*) P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Ferey, R. E. Morris and C. Serre, *Chem. Rev.*, 2012, **112**, 1232.

ChemComm Accepted Manuscript

2 (*a*) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105; (*b*) D. M. Liu, K. D. Lu, C. Poon and W. B. Lin, *Inorg. Chem.*, 2014, **53**, 1916; (*c*) J. Rocha, L. D. Carlos, F. A. A. Paz and D. Ananias, *Chem. Soc. Rev.*, 2011, **40**, 926.

3 (*a*) Y. J. Cui, Y. F. Yue, G. D. Qian and B. L. Chen, *Chem. Rev.*, 2012, **112**, 1126; (*b*) P. F. Shi, B. Zhao, G. Xiong, Y. L. Hou and P. Cheng, *Chem. Commun.*, 2012, **48**, 8231; (*c*) X. Q. Zhao, P. Cui, B. Zhao, W. Shi and P. Cheng, *Dalton Trans.*, 2011, **40**, 805.

4 (*a*) D. M. Liu, R. C. Huxford and W. B. Lin, *Angew. Chem. Int. Edit.*, 2011, **50**, 3696; (*b*) P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J. S. Chang, Y. K. Hwang, V. Marsaud, P. N. Bories, L. Cynober, S. Gil, G. Ferey, P. Couvreur and R. Gref, *Nat. Mater.*, 2010, **9**, 172; (*c*) K. E. Dekrafft, Z. G. Xie, G. H. Cao, S. Tran, L. Q. Ma, O. Z. Zhou and W. B. Lin, *Angew. Chem. Int. Edit.*, 2009, **48**, 9901.

5 J. Y. Han and K. Burgess, *Chem. Rev.*, 2010, **110**, 2709.

6 (*a*) H. L. Jiang, D. W. Feng, K. C. Wang, Z. Y. Gu, Z. W. Wei, Y. P. Chen and H. C. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 13934; (*b*) J. Aguilera-Sigalat and D. Bradshaw, *Chem. Commun.*, 2014, **50**, 4711; (*c*) B. V. Harbuzaru, A. Corma, F. Rey, J. L. Jorda, D. Ananias, L. D. Carlos and J. Rocha, *Angew. Chem. Int. Edit.*, 2009, **48**, 6476.

7 (*a*) J. Della Rocca, D. M. Liu and W. B. Lin, *Accounts Chem. Res.*, 2011, **44**, 957; (*b*) O. Shekhah, J. Liu, R. A. Fischer and C. Woll, *Chem. Soc. Rev.*, 2011, **40**, 1081.

8 (*a*) P. Li, L. B. Fang, H. Zhou, W. Zhang, X. Wang, N. Li, H. B. Zhong and B. Tang, *Chem-Eur. J.*, 2011, **17**, 10520; (*b*) T. Kuner and G. J. Augustine, *Neuron*, 2000, **27**, 447; (*c*) S. J. Hong, J. Yoo, S. H. Kim, J. S. Kim, J. Yoon and C. H. Lee, *Chem Commun.*, 2009, 189.

9 (*a*) B. K. McMahon and T. Gunnlaugsson, *J. Am. Chem. Soc.*, 2012, **134**, 10725; (*b*) T. Gunnlaugsson, J. P. Leonard, K. Senechal and A. J. Harte, *J. Am. Chem. Soc.*, 2003, **125**, 12062; (*c*) C. P. Mccoy, F. Stomeo, S. E. Plush and T. Gunnlaugsson, *Chem. Mater.*, 2006, 18, 4336.

10 (*a*) J. P. Leonard, C. M. G. dos Santos, S. E. Plush, T. McCabe and T. Gunnlaugsson, *Chem. Commun.*, 2007, 129; (*b*) C. S. Bonnet, J. Massue, S. J. Quinn and T. Gunnlaugsson, *Org. Biomol. Chem.*, 2009, **7**, 3074.

11 Y. Lu and B. Yan, *J. Mater. Chem. C*, 2014, **2**, 5526.

12 Y. Lu, B. Yan and J. L. Liu, *Chem. Commun.*, 2014, **50**, 9969.

13 E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 14382.

14 (*a*) Y. Y. Liu, R. Decadt, T. Bogaerts, K. Hemelsoet, A. M. Kaczmarek, D. Poelman, M. Waroquier, V. Van Speybroeck, R. Van Deun, P. Van Der Voort, *J. Phys. Chem. C* 2013, **117**, 11302; (*b*) Y. Lu and B. Yan, *J. Mater. Chem. C*, 2014, **2**, 7411.

15 K. Binnemans, *Chem. Rev.*, 2009, **109**, 4283.

16 (*a*) L. D. Carlos, R. A. S. Ferreira, V. D. Bermudez and S. J. L. CRibeiro, *Adv. Mater.*, 2009, **21**, 509; (*b*) B. Yan, *RSC Adv.*, 2012, **2**, 9304.

17 M. P. Hehlen, M. G. Brik, K. W. Kramer, *J. Lumin.*, 2013, **136**, 221.

18 (*a*) J. N. Hao and B. Yan, *Dalton Trans.*, 2014, **43**, 2810; (*b*) J. N. Hao and B. Yan, *New J. Chem.*, 2014, **38**, 3540.

19 (*a*) Z. Xiang, C. Fang, S. Leng and D. Cao, *J. Mater. Chem. A*, 2014, **2**, 7662; (*b*) D. Casanova, C. Bouzigues, T. L. Nguyen, R. O. Ramodiharilafy, L. Bouzhir-Sima, T. Gacoin, J. P. Boilot, P. L. Tharaux and A. Alexandrou, *Nat. Nanotechnol.*, 2009, **4**, 581.

20 Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815.

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