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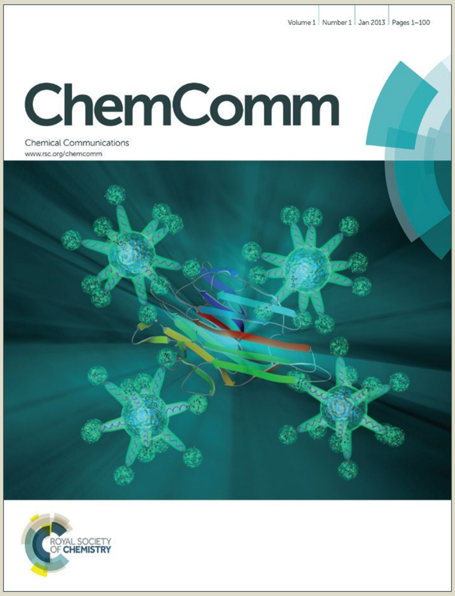

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# A Near Infrared Luminescent Metal–Organic Framework for Temperature Sensing in Physiological Range

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**A near infrared pumped luminescent metal-organic framework thermometer $Nd_{0.577}Yb_{0.423}BDC\text{-}F_4$, with near infrared fluorescence and excellent sensitivity in the physiological temperaturerange (293~313 K), has been first realized, and might be potentially applied for biomedical systems.**

Lanthanide metal–organic frameworks (Ln-MOFs), in view of the unique characteristics, including long luminescent lifetime, large Stokes shift, as well as the wide emission range from ultraviolet (UV) to near-infrared (NIR), have attracted tremendous attention.[1] The intrinsic luminescent features of lanthanides together with the unique advantages of MOFs offer excellent prospects for designing novel luminescent materials with enhanced desired functionalities and high added value for specific targeted applications. Recently, several mixed Ln-MOFs, with fast response and high sensitivity, have been realized and shown great potential to be excellent candidates for luminescent thermometer application.[2]

As is well known, the mixed Ln-MOF thermometers, which using the intensity ratio of two emissions from lanthanide ions (Tb/Eu) as the ratiometric thermometric parameter, make the temperature sensing independent of the concentration and inhomogeneity of luminescent centers as well as the optoelectronic drifts of excitation source and detectors, thus overcoming the main drawbacks of the intensity-based measurements of only one transition.[3] Recently, we have demonstrated the first ratiometric luminescent MOF thermometer, **$Eu_{0.0069}Tb_{0.9931}$-DMBDC** (DMBDC = 2,5-dimethoxy-1,4-benzendicarboxylate), based on the intensity ratio between emissions of $Tb^{3+}$ at 545 nm and $Eu^{3+}$ at 613 nm.[2a] This lanthanide MOF exhibits an excellent linear correlation between temperature and luminescence intensity ratio from 50 to 200 K. The basic principle revealed within the mixed lanthanide MOF indicates that such thermometer can also be applied in the physiological temperature range. Therefore, the NIR luminescent MOFs will be practically very useful because the generated NIR emission will have high permeability through biotissues and no competing fluorescence from biomatrices.[4] However, to the best of our knowledge, no NIR luminescent MOFs have been realized so far for the temperature sensing applications.

Some details, admittedly, must be concerned deliberately to exploit the NIR luminescent Ln-MOFs for biological temperature sensing. Firstly, the selected lanthanide ions with NIR luminescence as the metal ion sites of mixed Ln-MOF, such as $Yb^{3+}$ and $Nd^{3+}$, should be excited by NIR instead of the UV or visible light. Secondly, the organic ligand, with a much higher triplet energy level than the accepting level of lanthanide ions, as linker immobilization in the framework, can effectively decrease or prevent the energy transfer or interaction between the linker and lanthanide ions. Thirdly, some high energy chemical bonds, such as C-H, N-H, and O-H, should be excluded, since they can act as oscillators to significantly quench the NIR emission of lanthanide ions.[5] Based on these considerations, we select 2,3,5,6-tetrafluoro-1,4-benzenedicarboxylate ($H_2BDC\text{-}F_4$), with the triplet excited energy state of 27465 $cm^{-1}$ and weaker vibration bonds, as the organic linker to construct the new mixed Ln-MOF with the $Yb^{3+}$ and $Nd^{3+}$ ions. Obviously, the energy difference between the triplet excited energy of $H_2BDC\text{-}F_4$ and the accepting level of $Nd^{3+}$ or $Yb^{3+}$ is large enough to prevent their mutual interactions, and the C-F instead of the vibrational C-H bond in the benzene ring can effectively reduce the quenching effect of NIR luminescence of the ions, a property that is critical for our new mixed Ln-MOF.

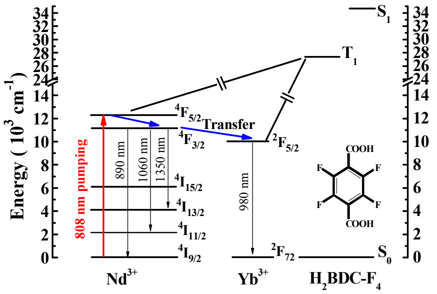

**Fig. 1** Schematic representation of energy processes in Ln-MOF.

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For reference, a schematic representation of energy transfer processes in our Ln-MOF is shown in Fig. 1. The idea is using the 808 nm laser to pump the $Nd^{3+}$ ions in their $^4F_{5/2}$ energy state, by taking advantage of inter conversion and the efficient nonradiation energy transfer from $Nd^{3+}$ to $Yb^{3+}$ ions, the emission around 980 nm for the $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition of $Yb^{3+}$ ions is obtained, and the characteristic NIR emissions around 890 nm, 1060 nm, and 1350 nm for the $^4F_{3/2}\rightarrow{}^4I_J$ (J = 13/2 11/2, 9/2) transitions of $Nd^{3+}$ are simultaneously observed.[6] This scheme is basically different with the well-known $Tb^{3+}$, $Eu^{3+}$ system where, however, the linker act as sensitizer that effectively transfer energy to the rare-earth ions under the UV irradiated. Under the 808 nm pumping, the emission intensity of $Nd^{3+}$ and $Yb^{3+}$ can exhibit the different trend due to the energy transfer efficiency from $Nd^{3+}$ to $Yb^{3+}$ ions would change with the temperature, thus the intensity ratio (Nd/Yb) can act as the ratiometric thermometric parameter to measure temperature. As expected, we synthesized a MOF $(Nd_{0.577}Yb_{0.423})_2(BDC\text{-}F_4)_3(DMF)(H_2O)\bullet DMF$ (**$Nd_{0.577}Yb_{0.423}BDC\text{-}F_4$**), with the excitation and emission band locate in NIR region, as a luminescent ratiometric thermometer for the measurement in physiological temperature range, and the nanorods of this sample also have been prepared for adequately application in the biological system.

The rod-like crystals $Nd_2(BDC\text{-}F_4)_3(DMF)(H_2O)\cdot DMF$ (**$NdBDC\text{-}F_4$**) and $Yb_2(BDC\text{-}F_4)_3(DMF)(H_2O)\cdot DMF$ (**$YbBDC\text{-}F_4$**) can be made by reacting $Nd(NO_3)_3\cdot 6H_2O$ or $Yb(NO_3)_3\cdot 5H_2O$ with $H_2BDC\text{-}F_4$, respectively. Moreover, the same synthetic procedures with varying the original molar ratio of $Nd(NO_3)_3$ to $Yb(NO_3)_3$ can be applied to prepare the **$Nd_{0.577}Yb_{0.423}BDC\text{-}F_4$**. The molar ratios of $Nd^{3+}/Yb^{3+}$ in the as-synthesized sample match with the original molar ratios of the corresponding lanthanide salt, and had been determined by inductively coupled plasma (ICP) analysis (Table. S1). Powder X-ray diffraction reveals that the resulting Ln-MOFs are isostructural to the reported $Er_2(BDC\text{-}F_4)_3(DMF)(H_2O)\cdot DMF$[7] (Fig. S1). The lanthanide ion is five-coordinate to four linking carboxylate groups from four ligands, the neighbouring ions are bridging by monodentate carbonyl of the $H_4BDC\text{-}F_4$ ligands, forming the three-dimensional structure.

Upon laser pumping at 808 nm, **$NdBDC\text{-}F_4$** exhibits the characteristic ($^4F_{3/2}\rightarrow{}^4I_J$, J =13/2, 11/2, 13/2) transitions of $Nd^{3+}$ around at 890 nm, 1060 nm and 1340nm, respectively. While no emission band around 980 nm ($^2F_{5/2}\rightarrow{}^2F_{7/2}$) for **$YbBDC\text{-}F_4$** was observed, which can be attributed to $Yb^{3+}$ has no absorption band around 808 nm (Fig. S3). Under the same condition, however, the mixed Ln-MOF **$Nd_{0.577}Yb_{0.423}BDC\text{-}F_4$** simultaneously displays the characteristic emissions of the $Nd^{3+}$ and $Yb^{3+}$ ions, implying efficient energy transfer from $Nd^{3+}$ to $Yb^{3+}$ ions and consisting with the proposed scheme.

We have investigated the temperature dependence of photoluminescence properties of the mixed Ln-MOF **$Nd_{0.577}Yb_{0.423}BDC\text{-}F_4$** in the physiological temperature range of 293~313 K. As illustrated in Fig. 2a, the intensity of $^2F_{5/2}\rightarrow{}^2F_{7/2}$ ($Yb^{3+}$, 980 nm) transition strongly enhances as the temperature increases , while the intensity of the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ ($Nd^{3+}$, 1060 nm) transition starts to increase until the temperature rises to 308 K. The inset of Fig. 2a clearly shows the temperature dependence for the normalized intensity of corresponding emissions. The change of $Nd^{3+}$ emission is different from the **$NdBDC\text{-}F_4$**, whose emission intensity is relatively stable over the whole temperature range (Fig. S4). Furthermore, the increase of the $Yb^{3+}$ emission is significantly different from **$YbBDC\text{-}F_4$**, which with no emission band excited at 808 nm. This phenomenon is a typical energy transfer process, which can be attributed to efficient energy transfer from the $Nd^{3+}$ to $Yb^{3+}$ ions and enhances with the increase in temperature based on thermally driven phonon-assisted transfer mechanism.

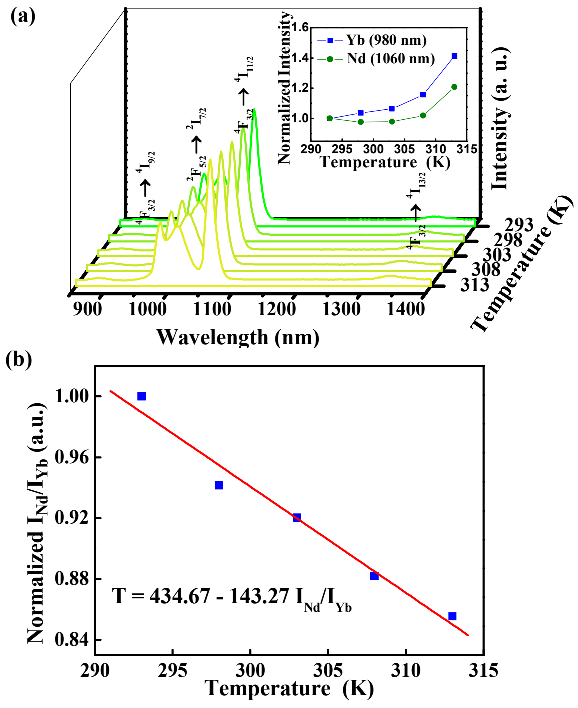

Fig. 2 (a) Emission spectra of **$Nd_{0.577}Yb_{0.423}BDC\text{-}F_4$** in the range of 293~313 K excited at 808 nm; inset: temperature dependence of the normalized intensity of corresponding transitions. (b) Temperature-dependent intensity ratio of $Nd^{3+}$ (1060 nm) to $Yb^{3+}$ (980 nm) and the fitted curve for **$Nd_{0.577}Yb_{0.423}BDC\text{-}F_4$**.

For the mixed Ln-MOF **$Nd_{0.577}Yb_{0.423}BDC\text{-}F_4$**, the intensity ratio of two emissions, the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ ($Nd^{3+}$, 1060 nm) and $^2F_{5/2}\rightarrow{}^2F_{7/2}$ ($Yb^{3+}$, 980 nm), can be applied as the thermometric parameter in ratiometric luminescent thermometers, allowing self-calibrating measurement of the temperature based on the emission spectra. As shown in Fig. 2b, the calibrate curve approximately follows a linear relationship between the $I_{Nd}/I_{Yb}$ ratio and temperature, which can be fitted as a function of

$$\mathrm{T} = 434.67 - 143.27\, I_{\mathrm{Nd}}/I_{\mathrm{Yb}} \qquad (1)$$

with a correlation coefficient $R^2$=0.966, which demonstrates that **$Nd_{0.577}Yb_{0.423}BDC\text{-}F_4$** is an excellent luminescent thermometer within the temperature range from 293 to 313 K. It is, to the best of our knowledge, the first one to use NIR as the light source, as well as, the intensity ratio of $Nd^{3+}$ and $Yb^{3+}$ transitions as the thermometric parameter for temperature detection among all luminescent MOF thermometers reported to date. To further assess the repeatability of the **$Nd_{0.577}Yb_{0.423}BDC\text{-}F_4$** thermometer, the temperature dependence of emissions were performed between 293 and 313 K for three cycles. The intensity ratios are nearly unchanged upon cycling the temperature (Fig. S5), thus indicating the excellent repeatability and reliability of this system.

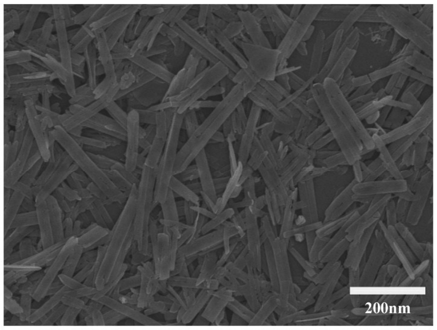

**Fig. 3** SEM image of nanoparticles for **Nd$_{0.577}$Yb$_{0.423}$BDC-F$_4$**.

The relative sensitivity is defined according with the reported thermometers,[2] and can be used to evaluate the performance of the **Nd$_{0.577}$Yb$_{0.423}$BDC-F$_4$** thermometer. The maximum sensitivity of **Nd$_{0.577}$Yb$_{0.423}$BDC-F$_4$** is 0.816% $K^{-1}$ at 313 K (Fig. S6), being almost two times higher than that of the mixed Ln-MOF $Tb_{0.99}Eu_{0.01}(BDC)_{1.5}(H_2O)_2$ which luminescence in visible area.[2e] In addition, the value of temperature measurement resolution for **Nd$_{0.577}$Yb$_{0.423}$BDC-F$_4$** (calculated on the basis of signal to noise ratios by spectrometer) is 0.029 K, that is precise enough to detect the temperature difference in major pathological cells, such as the brain tumour cells usually emerge 0.5~3.3 K disparity with normal surrounding tissue.[8] Thus, this thermometer might be potentially applied to the biomedical diagnosis.

To better employ this system for biomedical temperature measurement, we also prepared the nano-particles of **Nd$_{0.577}$Yb$_{0.423}$BDC-F$_4$** by a reverse microemulsion method. Briefly, adding $Na_2BDC-F_4$ or $Nd(NO_3)_3/Yb(NO_3)_3$ (molar ratio 1.36:1) to two separate CTAB/1-hexanol/isooctane/water microemulsions with W = 10 (W is defined as molar ratio of water-to-surfactant; CTAB = cetylmethylammonium bromide) and then stirred vigorously. When they were pellucid, the two microemulsions were combined and stirred vigorously for 1 h. After centrifugation and washed with ethanol for three times, the nano-particles of **Nd$_{0.577}$Yb$_{0.423}$BDC-F$_4$** were collected. As shown by the SEM image (Fig. 3), they are composed of crystalline nanorods with average diameter and length of 30 and 300 nm, respectively. Similarly, the prepared nano-particles of **Nd$_{0.577}$Yb$_{0.423}$BDC-F$_4$** also exhibit excellent temperature-dependent photoluminescent properties with maximum sensitivity of 1.201 %$K^{-1}$ at 313 K. (Fig.S7- S10)

In summary, we select the 2,3,5,6-tetrafluoro-1,4-benzenedicarboxylate with high energy level and weaker vibration bonds for synthesizing a novel thermosensitive mixed Ln-MOF **Nd$_{0.577}$Yb$_{0.423}$BDC-F$_4$**, which pumped by 808 nm laser and utilizes the intensity ratio of the $^4F_{3/2} \rightarrow ^4I_{11/2}$ ($Nd^{3+}$, 1060 nm) and $^2F_{5/2} \rightarrow ^2F_{7/2}$ ($Yb^{3+}$, 980 nm) transitions as a luminescent ratiometric thermometer for determining temperature. It shows excellent temperature-dependent photoluminescent properties around the physiological temperature range of 293~313 K, and gives relative sensitivity of 0.816% $K^{-1}$ at 313 K, even two times larger than its visible counterpart, $Tb_{0.99}Eu_{0.01}(BDC)_{1.5}(H_2O)_2$. **Nd$_{0.577}$Yb$_{0.423}$BDC-F$_4$**, with the NIR excitation and NIR luminescence, is harmless for the biological tissue, and the resolution is accurate for measure the temperature difference in major pathological cells, thus indicating this system can be potentially applied as a luminescent thermometer for biological sensing. We are currently concentrated on the engineering of applying the nanoparticles in biomedical diagnosis using infrared fluorescence imaging.

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