*Supporting Information*

# One Heterometallic {ZnEu}-Metal-Organic Framework for Efficient Chemical Fixation of $CO_2$

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**Table S1. Crystallographic data and refinement parameters of NUC-9**

| Complex | **NUC-9** |
|---|---|
| Formula | $C_{29}H_{11}EuNO_{13}Zn$ |
| Mr | 798.72 |
| Crystal system | trigonal |
| Space group | R-3m |
| a (Å) | 47.9882(19) |
| b (Å) | 47.9882(19) |
| c (Å) | 13.3456(10) |
| α (°) | 90 |
| β (°) | 90 |
| γ (°) | 120 |
| V(Å$^3$) | 26616(3) |
| Z | 18 |
| Dcalcd(g·cm$^{-3}$) | 0.897 |
| μ(mm$^{-1}$) | 1.491 |
| GOF | 1.116 |
| $R_1$ [I＞2σ(I)]$^a$ | 0.0599 |
| w$R_2$ [I＞2σ(I)]$^b$ | 0.1488 |
| $R_1{}^a$(all data) | 0.0688 |
| w$R_2{}^b$ (all data) | 0.1549 |
| $R_{int}$ | 0.0715 |

$^a R_1 = \sum \| |F_o| - |F_c| \| / \sum |F_o|$. $^b wR_2 = |\sum w(|F_o|^2 - |F_c|^2)| / \sum |w(F_o{}^2)^2|^{1/2}$

**Table S2. Selected bond lengths and angles**

| | | | | | |
|---|---|---|---|---|---|
| **NUC-9** | | | | | |
| Eu(1)-O(7) | 2.307(5) | Eu(1)-O(5)#5 | 2.480(5) | Eu(1)-O(4)#3 | 2.333(6) |
| Eu(1)-O(5)#4 | 2.480(5) | Eu(1)-O(7)#6 | 2.307(5) | Eu(1)-O(6)#4 | 2.428(5) |
| Eu(1)-O(1W) | 2.391(7) | Eu(1)-O(6)#5 | 2.428(5) | | |
| Zn(1)-O(2)#7 | 1.948(5) | Zn(1)-O(3) | 1.921(6) | O(8)-Zn(1)#3 | 1.970(5) |
| O(4) #5-Eu(1)-O(5)#3 | 124.71(16) | O(4) #5-Eu(1)-O(5)#4 | 124.72(16) | O(4) #5-Eu(1)-O(6)#3 | 74.40(16) |
| O(4) #5-Eu(1)-O(6)#4 | 74.40(16) | O(4)#5-Eu(1)-O(1W) | 150.2(3) | O(5)#3-Eu(1)-O(5)#4 | 82.3(4) |
| O(6)#4-Eu(1)-O(5)#3 | 102.5(2) | O(6)#3-Eu(1)-O(5)#4 | 102.5(2) | O(6)#3-Eu(1)-O(5)#3 | 51.54(17) |
| O(6)#4-Eu(1)-O(5)#4 | 51.54 (17) | O(6)#3-Eu(1)-O(6)#4 | 79.1(3) | O(7)#6-Eu(1)-O(4)#5 | 79.30(18) |
| O(7)-Eu(1)-O(5) #4 | 90.2(2) | O(7) -Eu(1)-O(5)#3 | 154.60(19) | O(7)6-Eu(1)-O(6)#3 | 153.6(18) |
| O(7)#6-Eu(1)-O(6)#3 | 91.4(2) | O(7)#6-Eu(1)-O(6)#4 | 153.56(18) | O(7) -Eu(1)-O(6)#4 | 91.4(2) |
| O(7)#6-Eu(1)-O(7) | 86.2(3) | O(7)#6-Eu(1)-O(1W) | 79.0(2) | O(7)-Eu(1)-O(1W) | 79.0(2) |
| O(1W)-Eu(1)-O(5)#3 | 75.59(19) | O(1W)-Eu(1)-O(5)#4 | 75.59(19) | O(1W)-Eu(1)-O(6)#4 | 126.4(18) |
| O(1W)-Eu(1)-O(6)#3 | 126.35(18) | O(4)#5-Eu(1)-O(5)#3 | 124.71(16) | O(4)#5-Eu(1)-O(5)#4 | 124.7(16) |
| O(4)#5-Eu(1)-O(6)#3 | 74.40(16) | O(4)#5-Eu(1)-O(6)#4 | 74.4(16) | O(4)#5-Eu(1)-O(1W) | 150.2(3) |
| O(3)-Zn(1)-O(8)#8 | 115.41(16) | O(3) -Zn(1)-O(8)#7 | 115.42(16) | O(3)-Zn(1)-O(2)#9 | 99.7(3) |
| O(8)#7-Zn(1)-O(8)#8 | 115.1(3) | O(2)#9-Zn(1)-O(8)#7 | 104.19(16) | O(2)#9-Zn(1)-O(8)#8 | 104.2(16) |
| Symmetry transformations used to generate equivalent atoms: #1 x,x-y+1,z; #2 x-y+2/3,x+1/3,-z+1/3 #3 y-1/3,y-x+1/3,-z+1/3; #4 -y+4/3,x-y+2/3,z-1/3; #5 -y+4/3,x-y+2/3,z-3; #6 -x+1,-y+1,z; #7 -x+y+2/3,-x+4/3,z+1/3; #8 y-x+2/3,-y+1/3,z+1/3; #9 -x+4/3,-y+5/3,-z+5/3. | | | | | |

**Table S3. The ICP measurement results.**

| Fluorescence experiment of **NUC-9** | initial | after sensing measurement |
|---|---|---|
| The concentration of $Fe^{3+}$ ($mol \cdot L^{-1}$) | $1\times10^{-2}$ | $9.980\times10^{-3}$ |

ICP measurements:

After the fluorescence experiment, the suspension was filtered. And filter cake (**NUC-9**) was washed with fresh solvent for several times. Then, ICP measurements were performed on the filtrate (solution containing Fe3+ ions), the results are listed in Table S3:

**Figure S1. The TGA curves of as-synthesized (black) and activated (red) sample of NUC-9.**

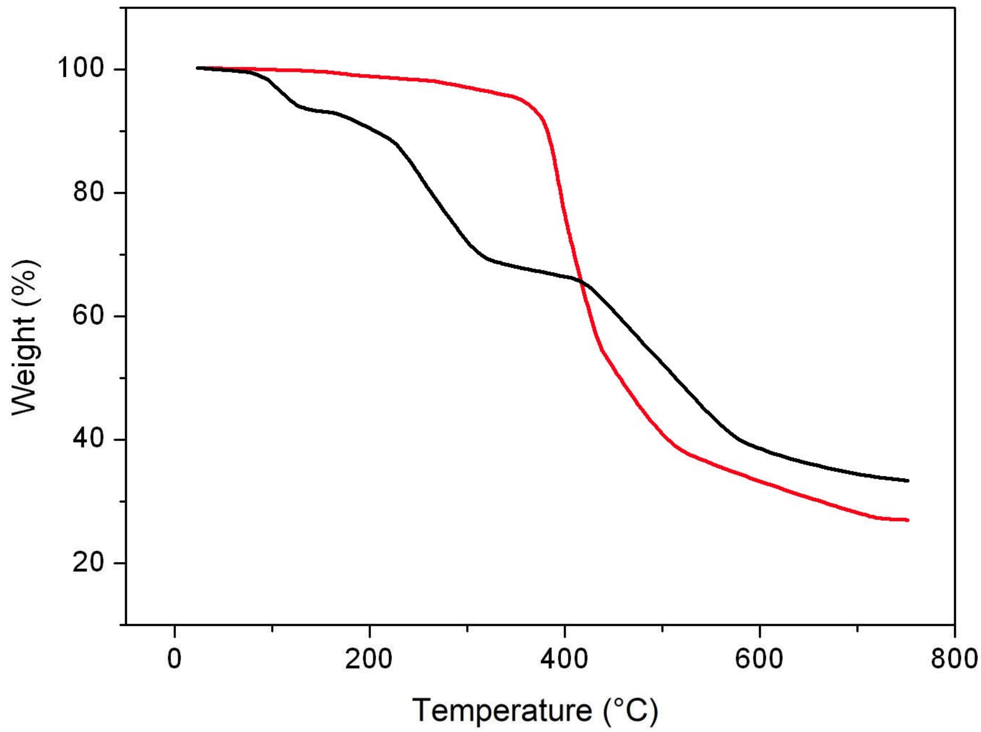

**Figure S2. PXRD patterns of NUC-9 under various treatments.**

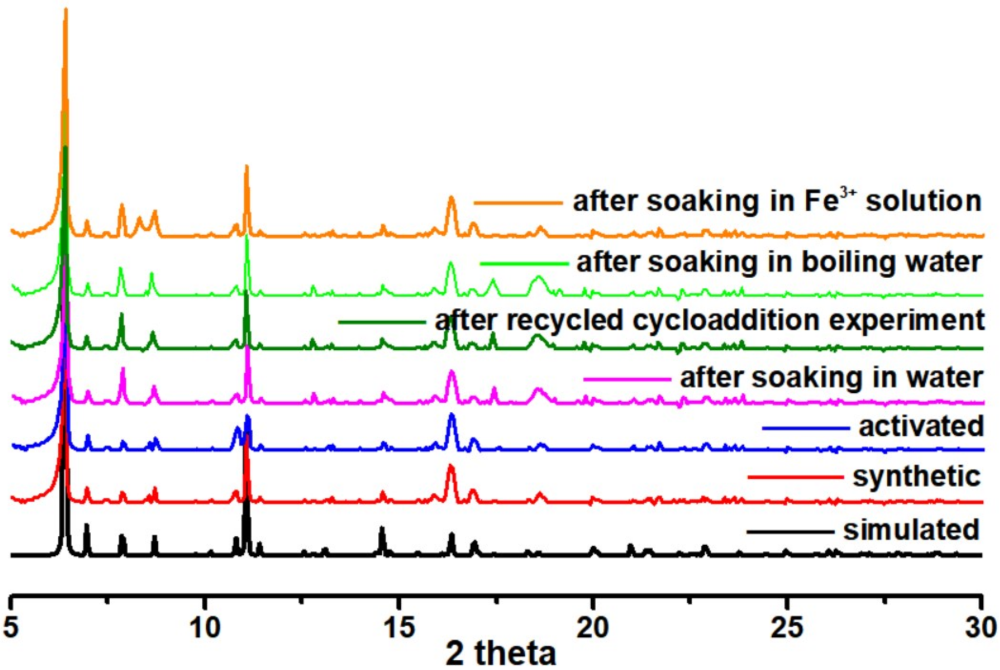

**Figure S3. $N_2$ absorption and desorption isotherms of NUC-9 at 77 K; inset: pore size distribution analyzed by NLDFT method.**

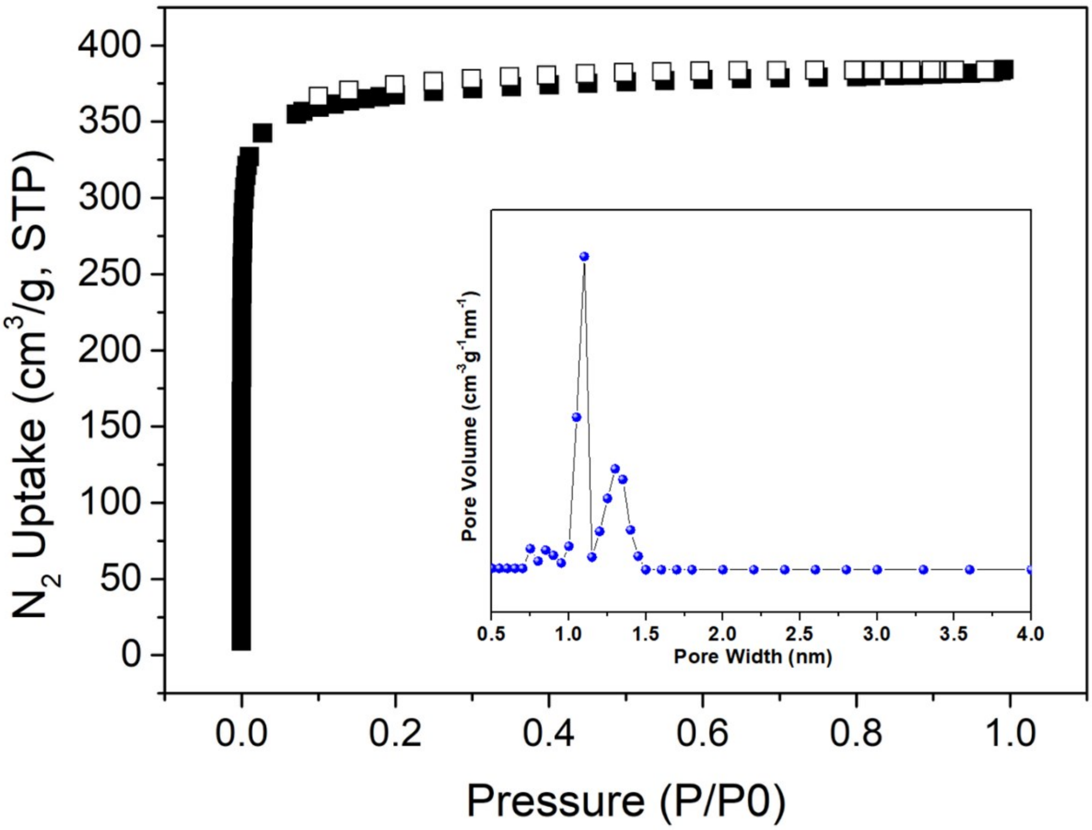

**Figure S4.** $CO_2$ **adsorption heat calculated by the virial equation of NUC-9**

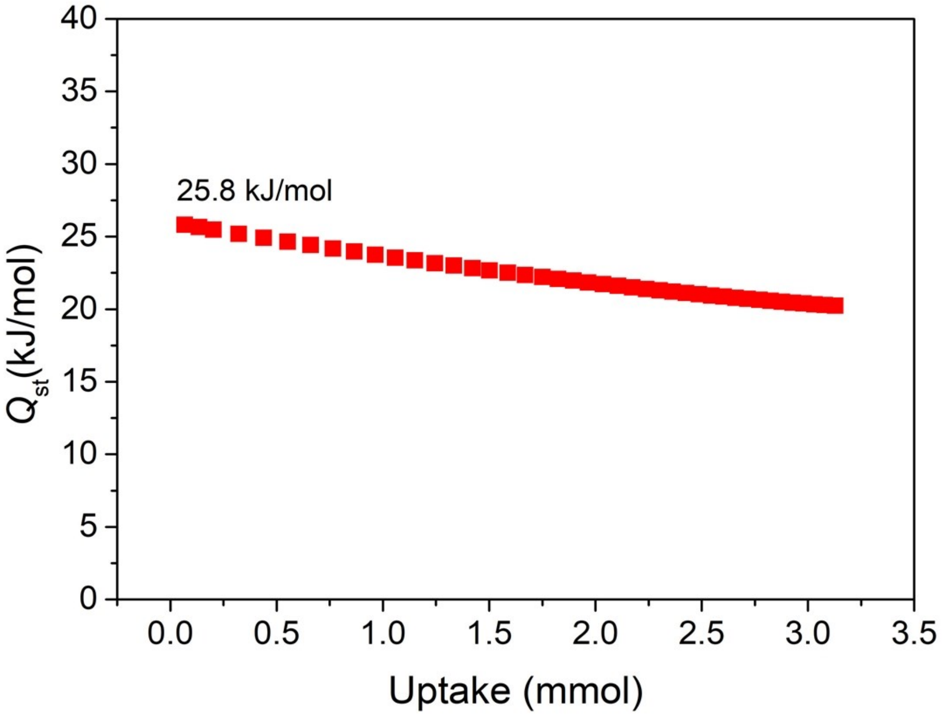

**Figure S5. Recyclability study (five cycles) for catalytic activities of NUC-9 in coupling of styrene oxide with $CO_2$**

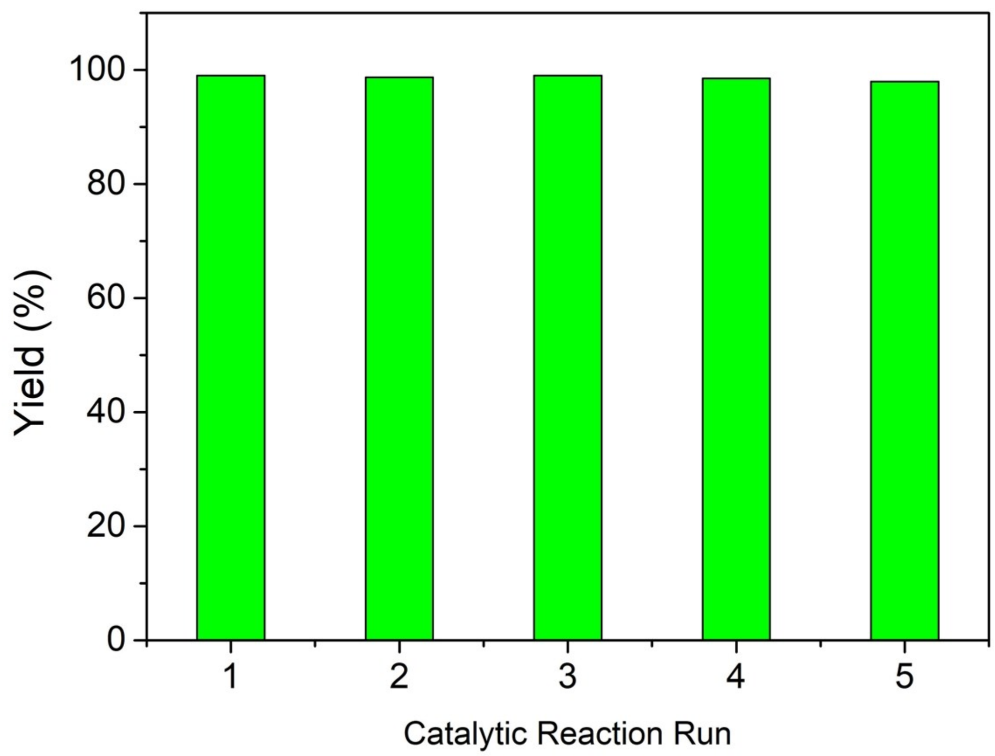

**Figure S6. Luminescence emissions of $H_6PTTBA$(a) and NUC-9 (b).**

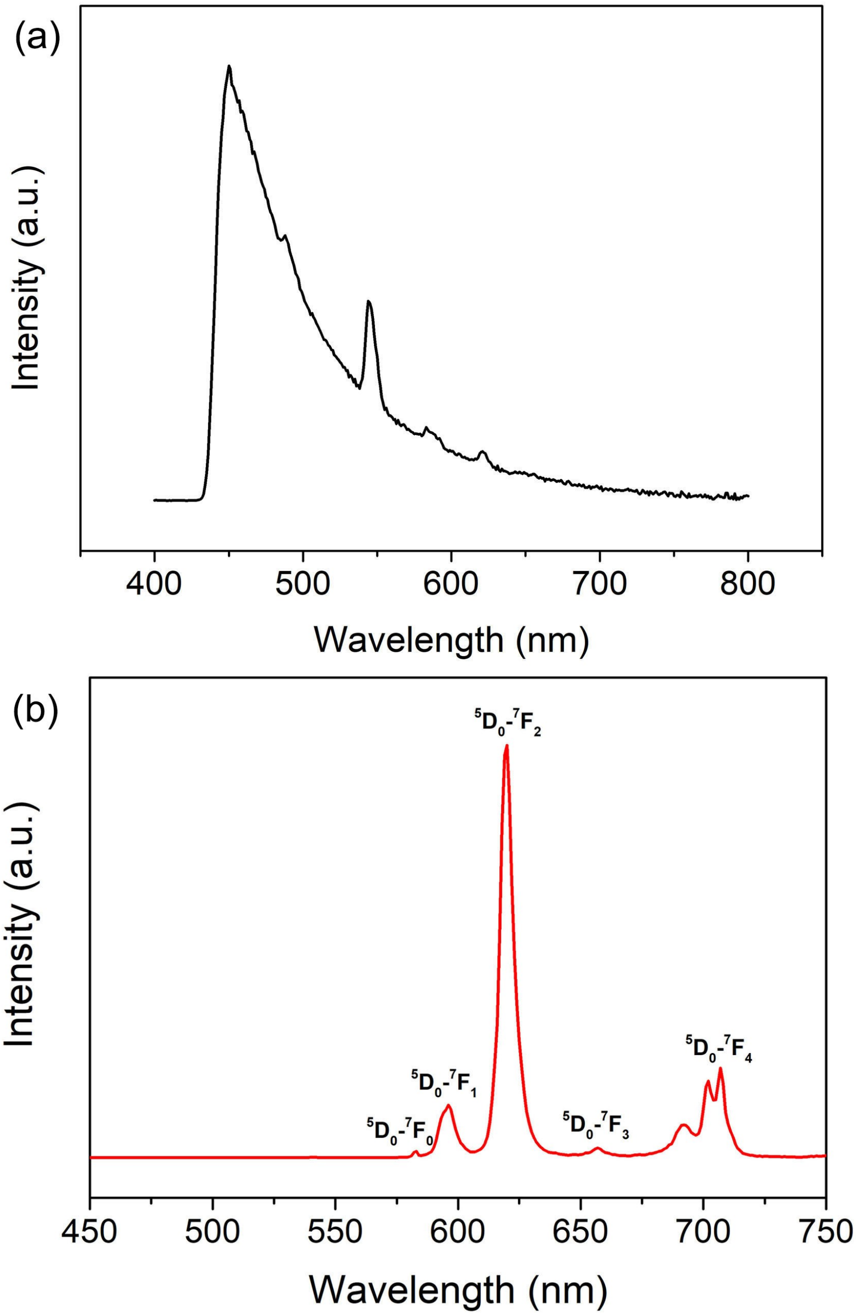

**Figure S7. Luminescence decay curve of NUC-9**

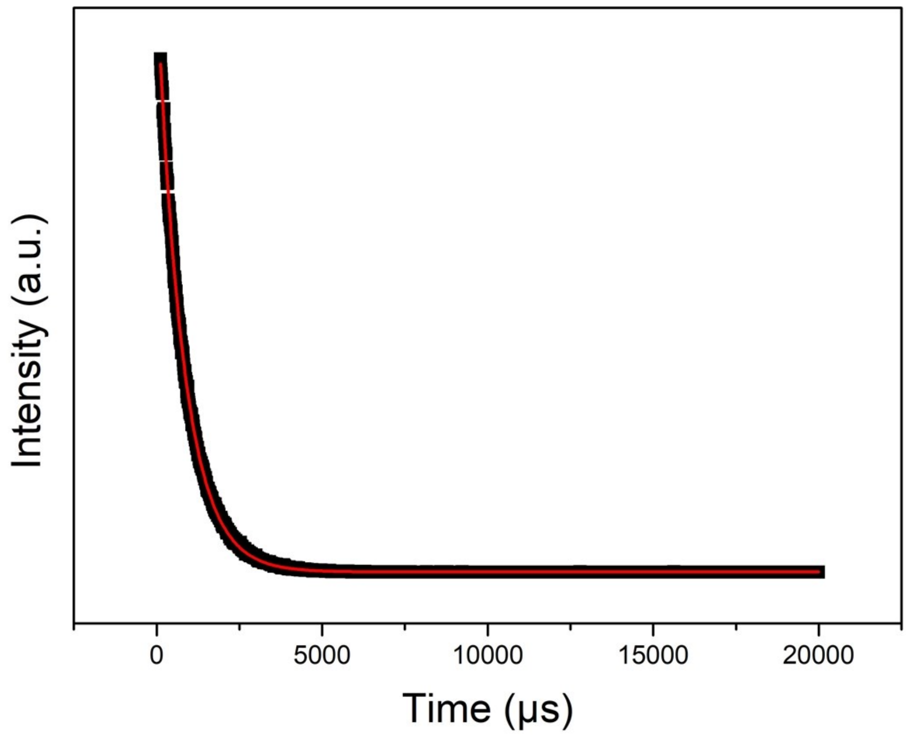

**Figure S8. Emission intensity NUC-9 suspensions with different metal ions in the absence (blue) and presence (brown) of $Fe^{3+}$**

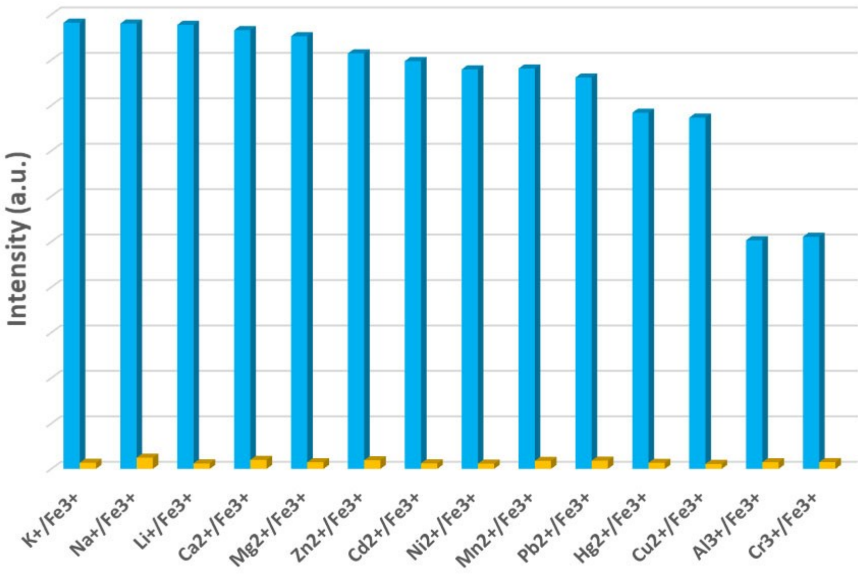

**Figure S9. Emission spectra of NUC-9 toward different concentration of $Fe^{3+}$ obtained from titration experiments.**

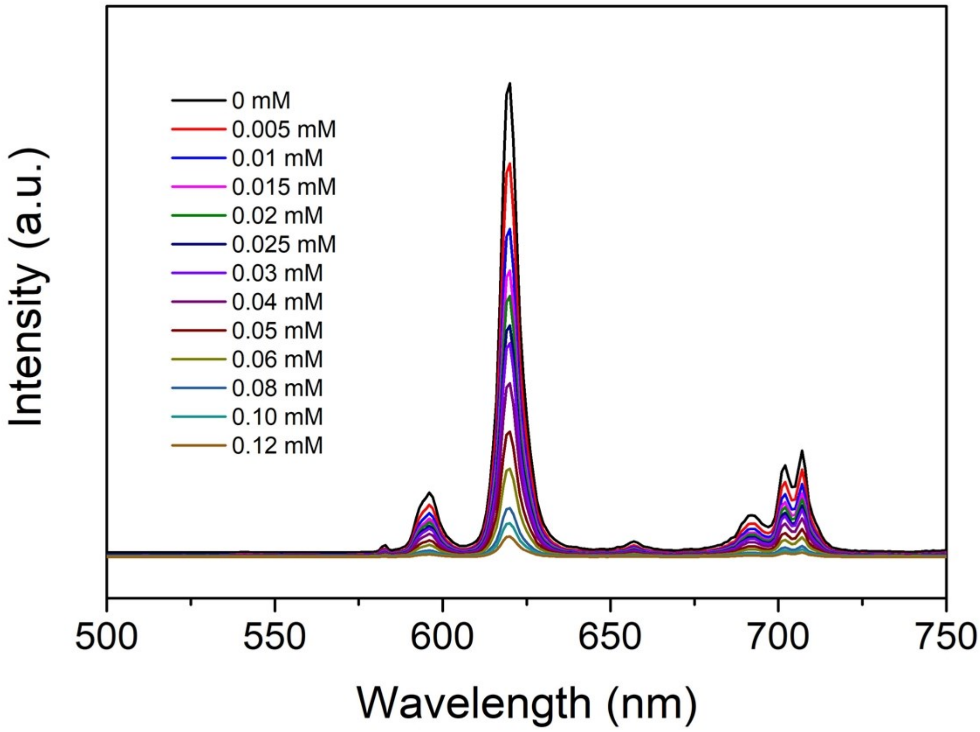

**Figure S10. Luminescence intensity ratio vs the concentration of $Fe^{3+}$ plot.**

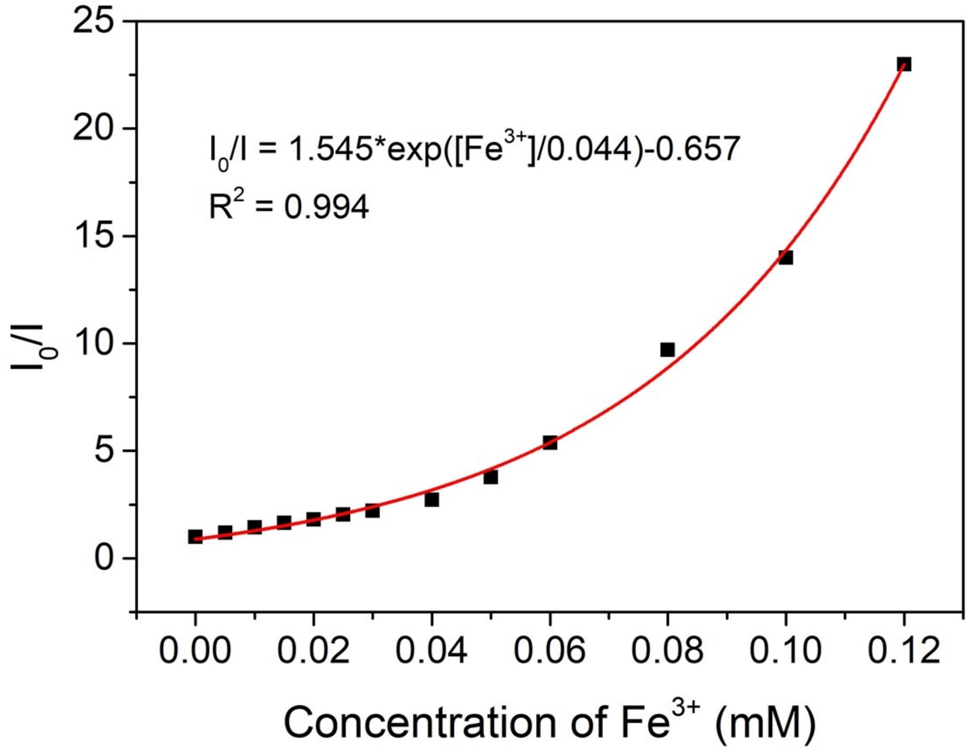

**Figure S11. The luminescence intensity ratio of NUC-9 versus $Fe^{3+}$ concentration in the range of 0 − 0.4 mM**

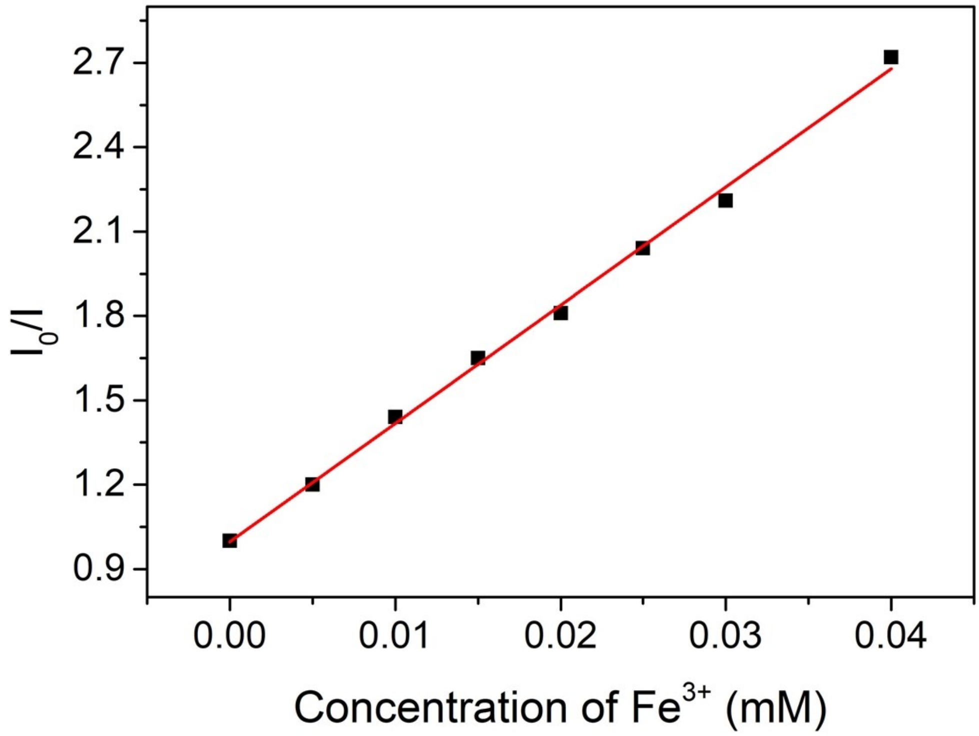

**Figure S12. The UV-Vis spectrum of $Fe^{3+}$ cation anion and NUC-9 in aqueous solution.**