SUPPORTING INFORMATION

A Porous 3D Heterometal-Organic Framework Containing Both Lanthanide and High-Spin Fe(II) Ions

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General Methods

Analyses for C, H and N were carried out on a Perkin-Elmer analyzer. PXRD were recorded on a rigakudmax 2500 diffractometer using Cu Kα radiation. Thermal gravimetric analyses were completed on a NETZSCH TG 209 instrument. Variable-temperature magnetic susceptibilities were performed on a Quantum Design MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms. The luminescent spectra were recorded on WGY-10 spectrometer. And the Mössbauer spectra were measured by an Oxford MS-500 model constant acceleration Mössbauer spectrometer with a 1024 multichannel analyzer. The velocity was calibrated by an α-Fe foil. The radiation source was ^{57}Co/Rh. A xenon (methane) proportional counter was used as a detector. Computer fits were performed to all measured data.

Crystal Structure Determination

Diffraction intensity data for single crystals of **1-3** were collected at room temperature on a Bruker Smart CCD diffractometer equipped with graphitemonochromated Mo*K*α radiation (λ = 0.71073 Å). The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.[1,2] Hydrogen atoms were located geometrically and refined isotropically. See the CIF file for details.

Crystal data for 2 and 3

For **2** (**$C_{21}H_{18}GdFe_{1.5}N_3O_{16.5}$**): M = 817.41, Hexagonal, *P6/mcc*, $a = b = 15.291(4)$ Å, $c = 15.573(7)$ Å,, $V = 3153.4(17)$ Å^3, $Z = 4$, $2\theta_{max} = 50.02°$, $T = 293(2)$ K, $R_{int} = 0.1206$, reflections collected/unique = 7195/948, GOF = 1.018, $R1[I>2\sigma(I)] = 0.0343$ and $wR2 = 0.0927$. Crystal data

for **3 (**$C_{21}H_{18}TbFe_{1.5}N_3O_{16.5}$): M = 819.07, Hexagonal, *P6/mcc*, $a = b = 15.199(2)$ Å, $c = 15.589(5)$ Å, $V = 3118.8(12)$ Å^3, $Z = 4$, $2\theta_{max} = 50.06°$, $T = 293(2)$ K, $R_{int} = 0.0550$, reflections collected/unique = 11486/948, GOF = 1.089, $R1[I>2\sigma(I)] = 0.0256$ and $wR2 = 0.0673$.

Table S1. Crystal data and structure refinement of 1-3

	1	**2**	**3**
Empirical formula	$C_{21}H_{18}EuFe_{1.5}N_3O_{16.5}$	$C_{21}H_{18}GdFe_{1.5}N_3O_{16.5}$	$C_{21}H_{18}TbFe_{1.5}N_3O_{16.5}$
Formula weight	812.12	817.41	819.07
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Monochromator	Graphite	Graphite	Graphite
Crystal System	Hexagonal	Hexagonal	Hexagonal
Space group	*P6/mcc*	*P6/mcc*	*P6/mcc*
Unit cell Dimensions	$a = b = 15.238(3)$ Å	$a = b = 15.291(4)$ Å	$a = b = 15.199(2)$ Å
	$c = 15.663(5)$ Å	$c = 15.573(7)$ Å	$c = 15.589(5)$ Å
	$\gamma = 120°$	$\gamma = 120°$	$\gamma = 120°$
Volume	3149.8(13) Å^3	3153.4(17) Å^3	3118.8(12) Å^3
Z	4	4	4
Density (calculated)	1.713 Mg/m^3	1.722 Mg/m^3	1.744 Mg/m^3
Absorption coefficient	2.728 mm^{-1}	2.839 mm^{-1}	3.012 mm^{-1}
$F(000)$	1596	1600	1604
θ	3.09 to 25.02°	3.08 to 25.01°	3.10 to 25.03°
Limiting indices	$-18 \le h \le 12$ $-4 \le k \le 18$ $-18 \le l \le 18$	$-5 \le h \le 18$ $-18 \le k \le 17$ $-17 \le l \le 17$	$-18 \le h \le 16$ $-12 \le k \le 18$ $-18 \le l \le 17$
Reflections collected / unique	8226 / 960 [R(int) = 0.0603]	7195 / 948 [R(int) = 0.1206]	11486 / 948 [R(int) = 0.0550]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	960 / 0 / 74	948 / 0 / 76	948 / 0 / 74
Goodness-of-fit on F^2	1.082	1.018	1.089
Final R indices $[I>2\sigma(I)]$	$R_1 = 0.0245$ $wR_2 = 0.0621$	$R_1 = 0.0343$ $wR_2 = 0.0927$	$R_1 = 0.0256$ $wR_2 = 0.0673$
R indices (all data)	$R_1 = 0.0468$ $wR_2 = 0.0733$	$R_1 = 0.0643$ $wR_2 = 0.1049$	$R_1 = 0.0422$ $wR_2 = 0.0742$
Largest diff. Peak and hole	1.014 and -0.569 e. Å^{-3}	1.311 and -0.398 e. Å^{-3}	1.054 and -0.320 e. Å^{-3}

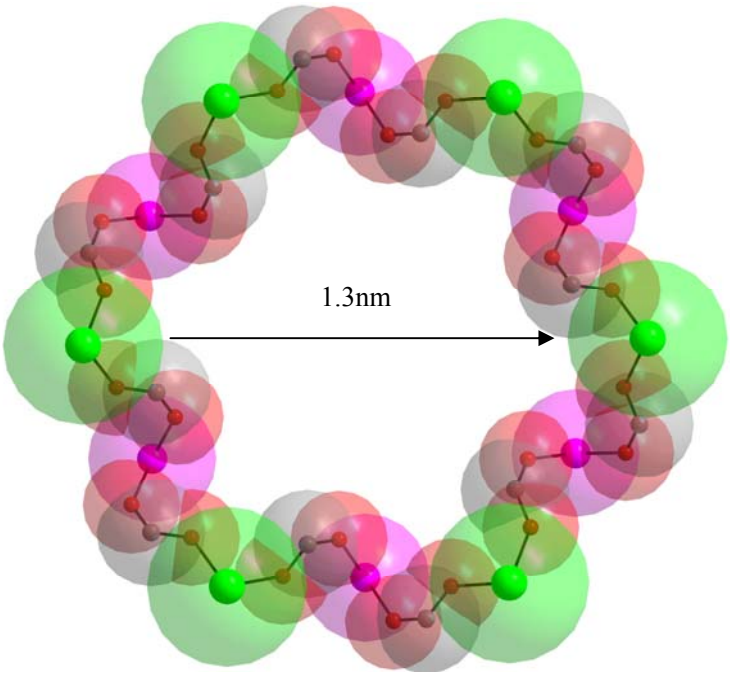

Figure S1. The space filling and ball-stick modes of the cross section of 1D tunnel in **1**. Color codes: green, Eu; grey, C; red, O; purple, Fe.

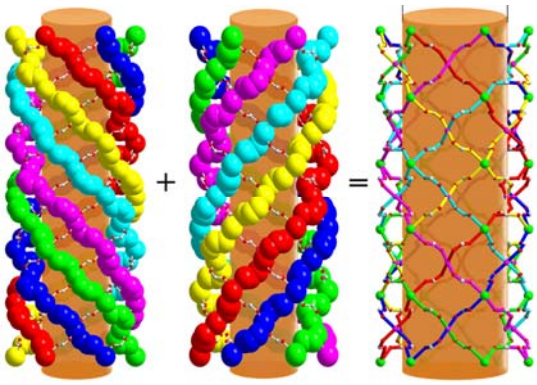

Figure S2. The wall of 1D channel was constructed by interweaving left- and right-hand sextuple-stranded helixes.

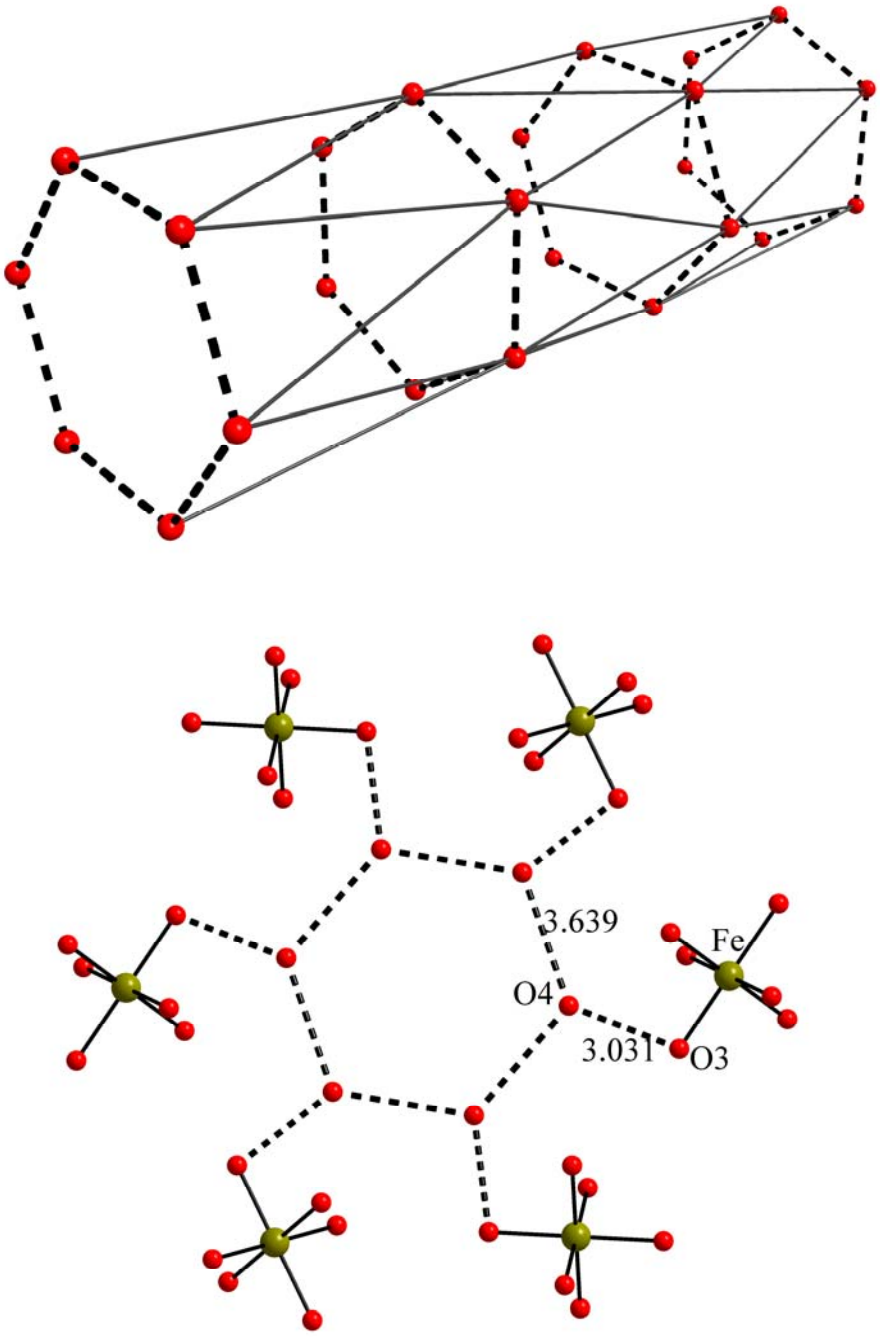

Figure S3. (Top) Side view of 'water pipe' in 1D channel with C_6 symmetry. (Bottom) The distance between adjacent water in the 1D channel, and hydrogen bonds between lattice water molecules and coordinated water on Fe^{2+}.

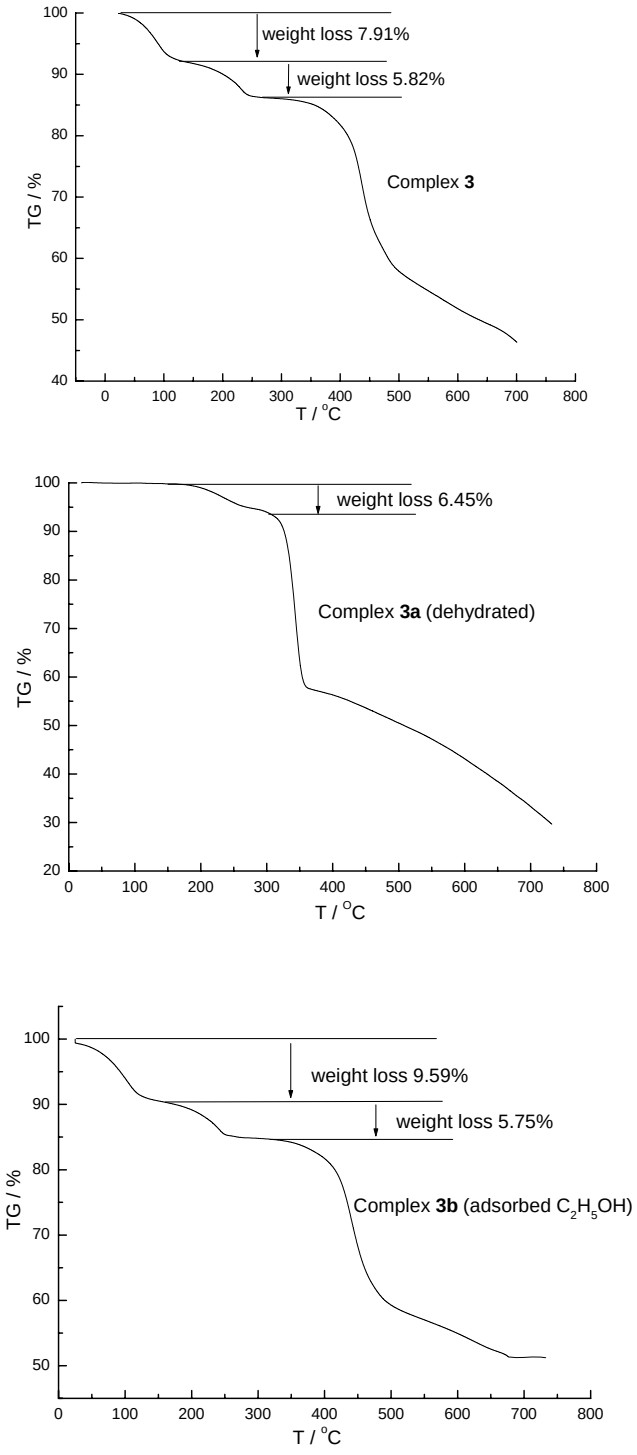

Figure S4. TG plots of complexes **3**, **3a** and **3b**.

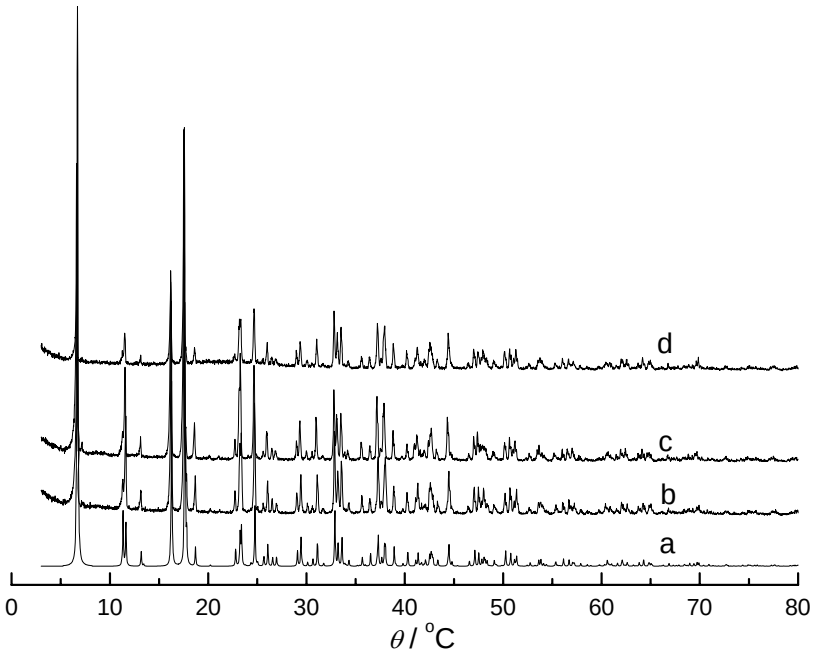

Figure S5. a) the simulated PXRD pattern for **3**; b), c) and d) corresponding to experimental ones for **3**, **3a** (dehydrated) and **3b** (adsorbed C_2H_5OH), respectively.

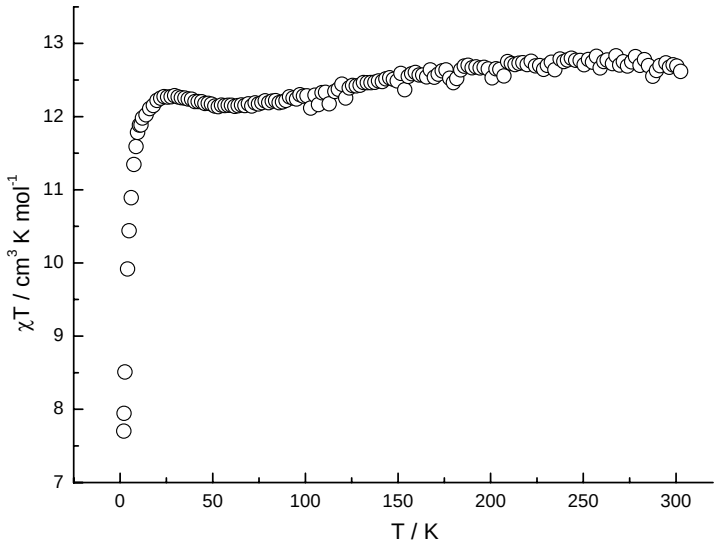

Figure S6. Plots of $\chi_M T$ versus T for **2.**

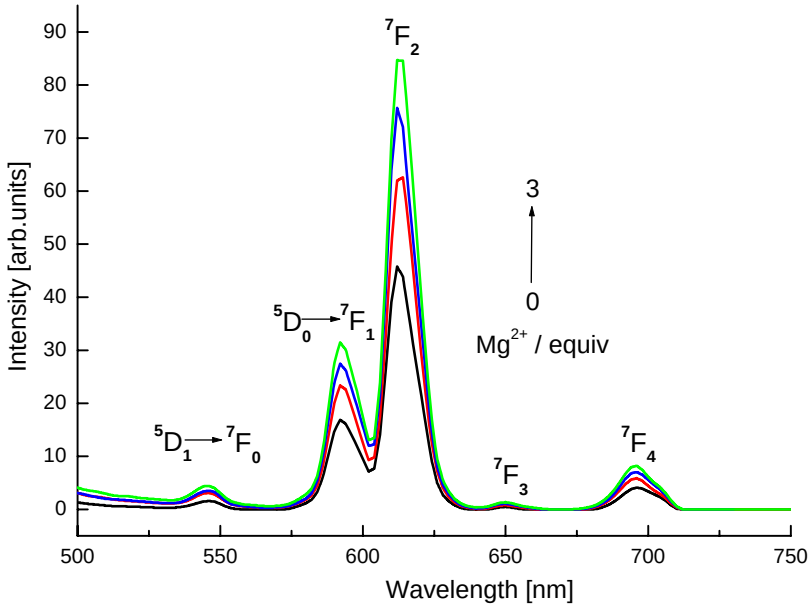

Figure S7. Emission spectra of complex **1** in DMF at RT (excited at 304 nm) in the presence of various concentrations of Mg^{2+} ($MgCl_2$) ions: 0 ~ 3 equivalents Mg^{2+} ions with respect to complex **1**. Color codes: black, no addition; red, one equivalent; blue, two equivalents; green, three equivalents.

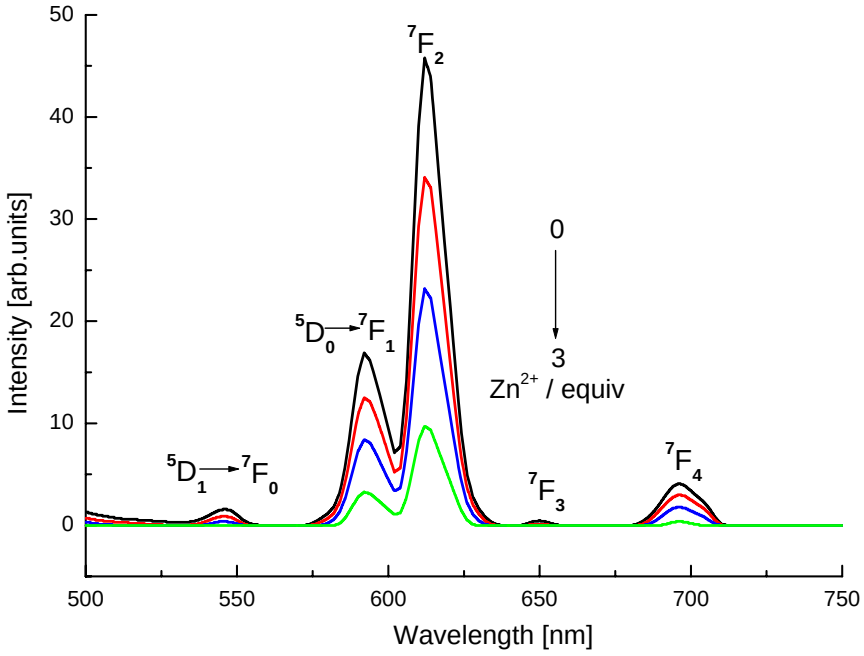

Figure S8. Emission spectra of complex **1** in DMF at RT (excited at 304 nm) in the presence of various concentrations of Zn^{2+} ($ZnCl_2$) ions: 0 ~ 3 equivalents Zn^{2+} ions with respect to complex **1**. Color code: black, no addition; red, one equivalent; blue, two equivalents; green, three equivalents

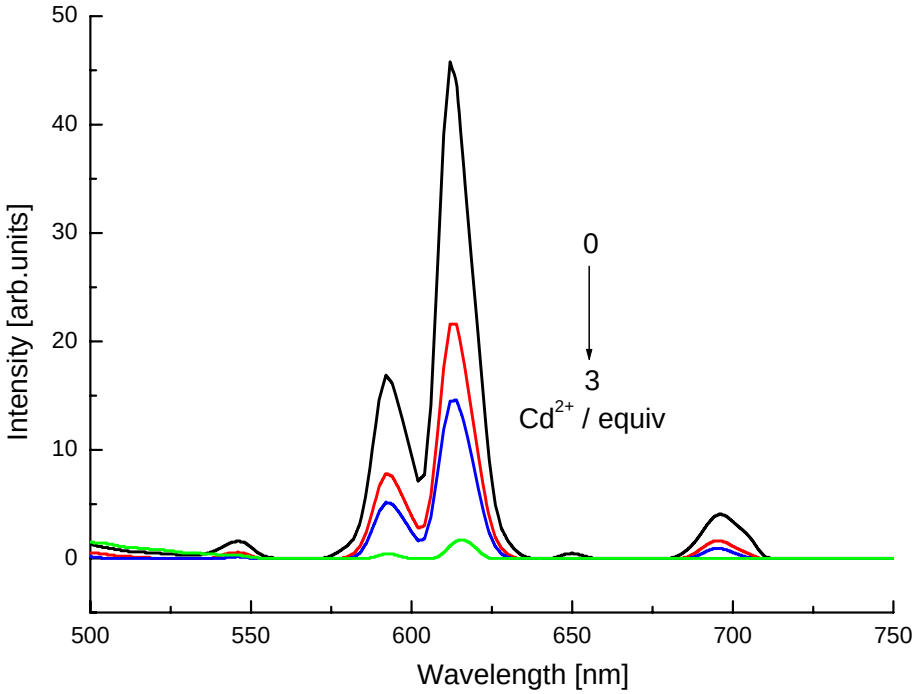

Figure S9. Emission spectra of complex **1** in DMF at RT (excited at 304 nm) in the presence of various concentrations of Cd^{2+} ($CdCl_2$) ions: 0 ~ 3 equivalents Cd^{2+} ions with respect to complex **1**. Color code: black, no addition; red, one equivalent; blue, two equivalents; green, three equivalents.

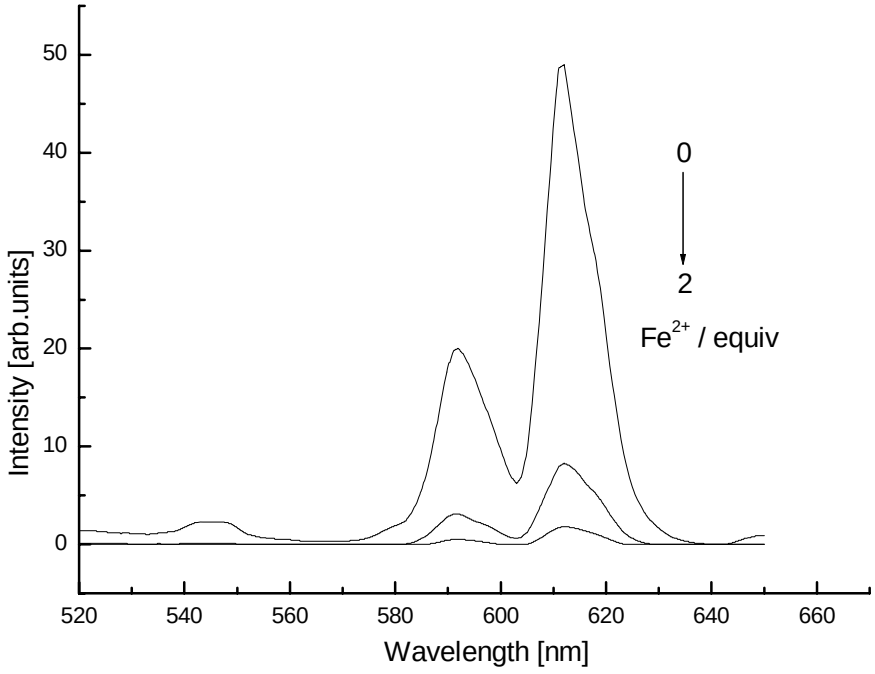

Figure S10. Emission spectra of complex **1** in DMF at RT (excited at 304 nm) in the presence of various concentrations of Fe^{2+} ($FeCl_2$)ions: 0 ~ 2 equivalents Fe^{2+} ions with respect to complex **1**.

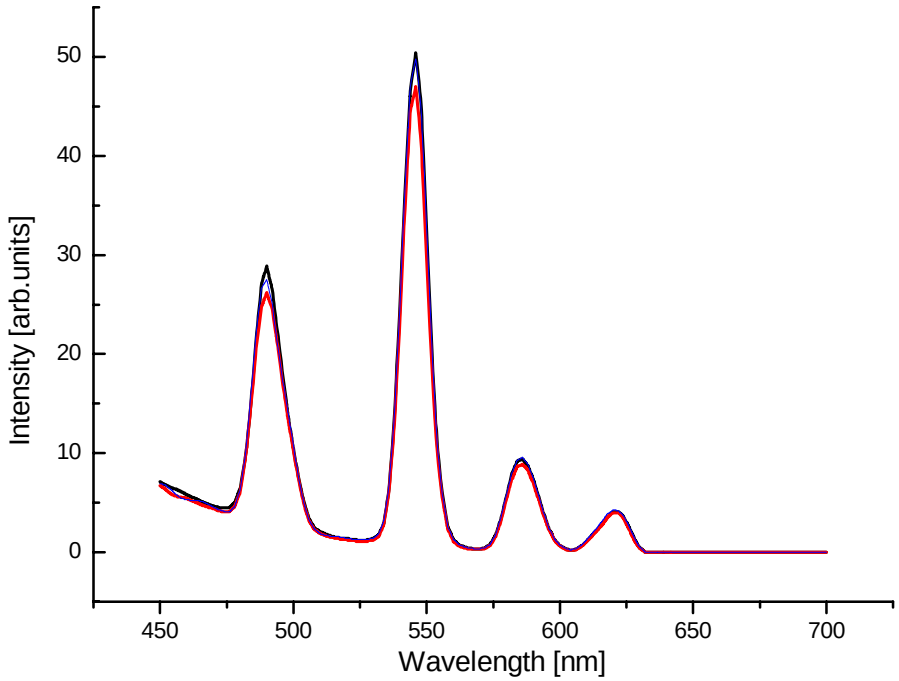

Figure S11. Emission spectra of complex **3** in DMF at RT (excited at 311 nm) in the presence of various concentrations of Mg^{2+} ($MgCl_2$) ions: 0 ~ 2 equivalents Mg^{2+} ions with respect to complex **3**. Color code: black, no addition; red, one equivalent; blue, two equivalents.

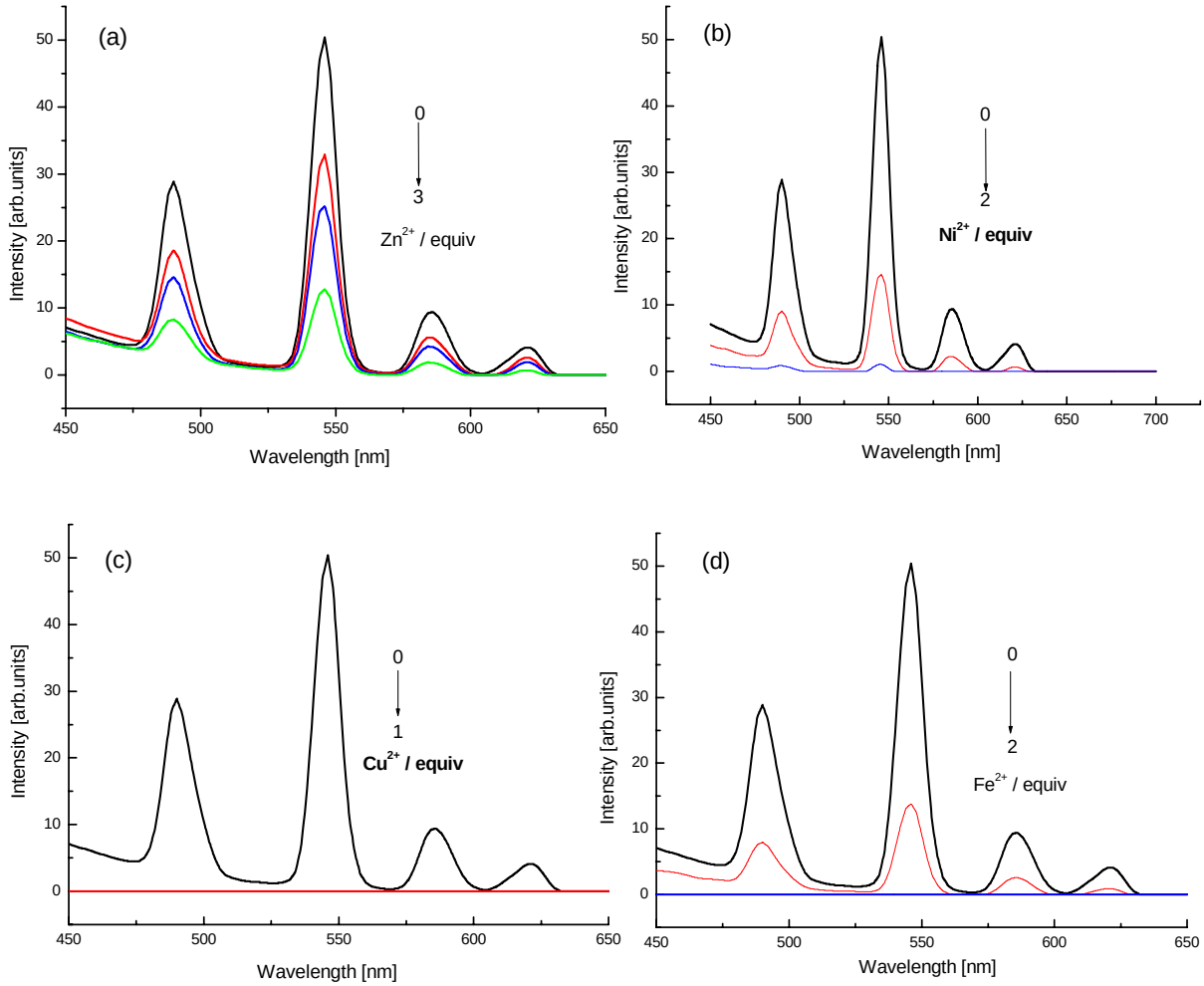

Figure S12. Emission spectra of complex **3** in DMF at RT (excited at 311 nm) in the presence of various concentrations of MCl_2 (M = Zn, (a); Ni, (b); Cu, (c); Fe, (d)) ions: 0 ~ 3 equivalents M^{2+} ions with respect to complex **3**. Color code: black, no addition; red, one equivalent; blue, two equivalents; green, three equivalents.

References

(1) Sheldrick, G. M. *SHELXS 97, Program for the Solution of Crystal Structures*; University of Göttingen: Germany, **1997**.

(2) Sheldrick, G. M. *SHELXL 97, Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, **1997**.