Supporting Information for

Rotation Restricted Emission and Antenna Effect in Single Metal-Organic Frameworks

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1. Reagents

Vitamin B1, methyl 4-formylbenzoate, 2, 5-dimethyl pyrazine and benzoin were purchased from Heowns Biochemistry Technology Co., Ltd., Tianjin, China. Tetrakis(4-carboxyphenyl)ethylene was get from Dibai Chemicals Technology Co., Ltd., Shanghai, China. Europium(III) nitrate hexahydrate (Eu(NO$_3$)$_3$·6H$_2$O), terbium(III) nitrate hexahydrate (Tb(NO$_3$)$_3$·6H$_2$O), and gadolinium(III) nitrate hexahydrate (Gd(NO$_3$)$_3$·6H$_2$O), glycine, alanine, leucine, isoleucine, valine, glutamine, cysteins, threonine, serine, phenylalanine, tyrosine, asparagine, methionine, glutamic, histidine, aspartic acid, glutamine, lysine, tryptophan, arginine were obtained from Sigma−Aldrich, Shanghai, China. Terephthalic acid was get from Guangfu Fine Chemistry Graduate School, Tianjin, China. Ammonium acetate was obtained from Macklin Biochemistry Co., Ltd., Shanghai, China. Sodium hydroxide was obtained from Beifangtianyi Chemistry Co., Ltd., Tianjin, China. N, N′-dimethylacetamide, concentrated hydrochloric acid and tetrahydrofuran were purchased from Concord Chemical Research Institute (Tianjin, China).

All the chemicals were obtained at least of analytical grade and used without further purification. Ultrapure water was prepared with an Aquapro system (18.25 MΩ cm).

2. Instrumentations

UV-Vis absorption spectrum was recorded by a UV-3900-visible spectrophotometer, Hitachi, Japan. The steady-state fluorescence experiments were performed on a FL-4600 Fluorescence Spectrometer, Hitachi, Japan, equipped with a plotter unit and a quartz cell (1 cm × 1 cm). Infrared spectra (IR) were obtained by Bruker TENSOR 27 Fourier transform infrared spectroscopy. Thermogravimetric analysis (TGA) was performed on a PTC-10AIF-DTA analyzer heated from 20 °C at a ramp rate of 15 °C min$^{-1}$ under air. Transmission electron microscopy (TEM) images was recorded with TecnaiG2 F20, FEI Co. (America) operated at an accelerating voltage of 200 kV. Scanning Electron Microscopy (SEM) images were recorded with JSM-7500F, Japan. N$_2$ adsorption-desorption isotherm was performed with ASAP2020/Tristar 3000 surface area and pore analyzer at 274 K. PXRD patterns were recorded on a D/max-2500 diffractometer (Rigaku, Japan) using Cu Kα radiation (λ = 1.5418 Å) with a scanning speed of 8° min$^{-1}$ and a step size of 0.02° in 2θ. NMR experiments were performed on AV 400, Bruker, America. Elemental analysis was carried out on a vario EL CUBE analyzer (Elementary, Germany). The LC-MS data were obtained from the Agilent 1200 HPLC system coupled with an Agilent 6140 Quadrupole MS system (Santa Clara, CA).

3. Synthesis

3.1 Synthesis of 2, 3, 5, 6-Tetrakis(4-(methoxycarbonyl)phenyl)pyrazine

The synthesis of L1 was followed previous report with some modification. Vitamin B1 (0.9 g, 2.675 mmol) was added to the mixture of methanol and water (3:1) under ice bath. Then, sodium hydroxide solution (2.5 mL, 2M) was added in the above solution drop-wise in 5 min. Under rigid stir, methyl 4-formylbenzoate (7.45g, 45.5 mmol) was added into the above solution. After homogeneous solution was obtained, the reaction mixture was heated at 60 °C for 15 min and at 64-65 °C for 1 h. After cooling and filtering, the product dimethyl4, 4′-(1-hydroxy-2-oxoethane-1, 2-diyl) dibenzoate was obtained followed with washed by water, methanol and diethyl ether,
respectively, drying at 60 °C.²

Acetic anhydride (765 mg, 7.50 mmol) was added into the mixture of dimethyl 4, 4’-(1-hydroxy-2-oxoethane-1, 2-diyldibenzoate (1.64 g, 5.00 mmol) and ammonium acetate (1.155 g, 15.00 mmol) in 5 mL of acetic acid. After being heated for 12 h at 120 °C under N₂. After natural cooled to room temperature and water added into the above solution, the product became faint yellow solid. Then, dichloromethane was added to get solution. Water was used to wash the products for three times. The dichloromethane solution was evaporated to get orange solid. Finally, the pure light yellow 2, 3, 5, 6-tetrakis(4-(methoxycarbonyl)phenyl)pyrazine was obtained by filtering and washing with diethyl ether.¹¹H NMR (300 MHz, CDCl₃): δ = 8.06 (dt, J₁ = 9.0 Hz, J₂ = 2.1 Hz, 8H), 8.45 (dt, J₁ = 8.7 Hz, J₂ = 1.8 Hz, 8H), 3.94 (s, 12H).

¹³C NMR (75 MHz, CDCl₃): δ = 166.6, 148.2, 142.0, 130.6, 129.9, 129.7, 52.5.

Elemental analysis for C₃₆H₂₈N₂O₈: C 70.03%, H 4.56%, and N 4.65%.

3.2 Synthesis of 2, 3, 5, 6-Tetakis(4-carboxyphenyl)pyrazine (L1)

Sodium hydroxide (1.021g, 1.66 mmol) was added into 2, 3, 5, 6-tetrakis(4-(methoxycarbonyl)phenyl)pyrazine solution (30 mL, THF:H₂O 1:1), 75 °C reflux for 12 h. Then, THF was evaporated. The solution was acidified to pH 4−5 with HCl (2 M). The precipitate was filtered after washed with H₂O and dry at 60 °C to obtain faint yellow powder (0.88 g, 1.57 mmol). Elemental analysis for L1 C₃₂H₂₀N₂O₈: C 68.55%, H 3.60%, and N 5.01%.

¹¹H NMR (300 MHz, DMSO-d₆): δ = 13.11 (br, 4H), 7.94 (d, J = 8.4 Hz, 8H), 7.59 (d, J = 8.4 Hz, 8H).

¹³C NMR (75 MHz, DMSO-d₆): δ = 166.8, 148.2, 141.4, 131.1, 129.9, 129.3.

3.3 Synthesis of tetraphenylpyrazine³

The synthesis of tetraphenylpyrazine was accorded to the reported method with some modification. 2.00 g (10 mmol) of benzoin, 1.45 mL (15 mmol) of acetic anhydride, 2.35 g (30 mmol) of ammonium acetate and 10 mL acetic acid were added into a 50 mL round bottom flask. After being sonicated for 5 min under protect of N₂, the system refluxed for 4 h at 120 °C. The mixture was cooled down to room temperature and then filtered, washed by ice acetic acid and dry at 60 °C.

3.4 Synthesis of L1-Eu MOF

Crystal: Eu(NO₃)₃·6H₂O (18.3 mg, 0.04 mmol) and L1 (6.0 mg, 0.01 mmol) were dissolved in the mixture of N, N’-dimethylacetamide (DMF 1.5 mL), ethanol (0.5 mL) and pure water (0.5 mL). The as-obtained mixture was transferred to a stainless steel Teflon-lined autoclave of 30 mL capacity. After being sonicated for 5 min under protect of N₂, the system refluxed for 4 h at 120 °C. The mixture was cooled down to room temperature and then filtered, washed by DMF to remove the residual L1 and Eu³⁺ ions. Finally, the samples were dried under 50 °C. IR (cm⁻¹): 3438(m), 2905(w), 1596(s), 1553(s), 1393(s), 1185(w), 1139(m), 1087(m), 999.54(m), 852(m), 789(m), 737(m), 709(w), 536(w).

The preparation methods of L1-Eu MOF with different morphology were illustrated in Table S2.

3.5 Synthesis of L1-Gd MOF and L1-Tb MOF

The synthesis of L1-Gd MOF and L1-Tb MOF was similar to that of L1-Eu MOF, only replace
Eu(NO$_3$)$_3$·6H$_2$O with Gd(NO$_3$)$_3$·6H$_2$O (18.6 mg, 0.04 mmol) or Tb(NO$_3$)$_3$·6H$_2$O (18.7 mg, 0.04 mmol), respectively.

3.6 Synthesis of L2-Eu MOF

Eu(NO$_3$)$_3$·6H$_2$O (18.3 mg, 0.05 mmol) and tetrakis(4-carboxyphenyl)ethylene (L2, 5.0 mg, 0.01 mmol) were dissolved in DMF (2 mL). The as-obtained mixture was transferred to a stainless steel Teflon-lined autoclave of 30 mL capacity. After sonicated for 5 min, the mixture was maintained at 393 K for 24 h under static condition. After naturally cooling to room temperature, the solution was removed by centrifugation and the material was washed with DMA and ethanol to remove the residual ligand and EuCl$_3$.

3.7 Synthesis of L3-Eu MOF

The synthesis method of L3-Eu MOF was similar to L1-Eu MOF, only replace the L1 with L3 (terephthalic acid, 5.0 mg, 0.03 mmol).

4. Methods

4.1 Limit of detection

According to the International Union of Pure and Applied Chemistry (IUPAC), the detection limit is calculated with followed formula.

\[
\text{LOD} = kS_b/a
\]

Where LOD is limit of detection, k=3 for spectral chemical analysis, and a is the sensitivity of a sensor (i.e. the slope of the calibration curve). The confidence level corresponding to k = 3 is about 90%. S$_b$ is the standard deviation of the blank signal.

4.2 The energy collection of single state ($S_1$) energy and triplet state ($T_1$)

The $S_1$ is related to the absorbance of a ligand, so $S_1$ was obtained from the UV-vis spectrum of ligands. $T_1$ is the triplet state of a ligand and phosphorescence is observed when the electron transfer from the triplet state to ground state. Once a ligand is coordinated to Ln$^{3+}$ ions, the triplet state is induced through intersystem crossing. Because the excited state of Gd$^{3+}$ ions has a higher energy than the triplet state of most ligands, no sensitization of Gd$^{3+}$ ions occurs in the Gd MOFs. The phosphorescence from ligand-Gd MOFs was measured at 77K. The energy of the phosphorescence is recorded as $T_1$. $T_1$ energy of a ligand can be determined precisely with the phosphorescence from the ligand-Gd MOFs at 77K. However, once the reaction was started, the process and the low temperature (such as 77K) are difficulty controlled. There is no difference between the 77K and room temperature emission for the L2-Gd MOF as we detected. Hence, the $T_1$ values of L2 are estimated from the emission before and after L2 reacts to Gd$^{3+}$ ions.
5. Figures and Tables

**Figure S1.** Fluorescence profile of L1 in DMF.

**Figure S2.** UV-Vis absorption spectra of (a) L1-Eu, (b) L1-Tb and (c) L1-Gd systems for different reaction time.
**Figure S3.** The fluorescence profile of solid state L1.

**Figure S4.** The time-dependent $^1$H NMR spectra of L1 in the presence of Eu$^{3+}$ ions. The characteristic peak at 13 ppm becomes lower and lower for –COOH on L1 because of coordination interaction.
**Figure S5.** The emission enhancement of Ln$^{3+}$ ions along with the reaction in different L1-Ln$^{3+}$ system. $I$ is the fluorescence intensity of the Ln$^{3+}$ ions and $I_0$ is the intensity of the ions at 20 seconds after the mixing of L1 and Ln$^{3+}$ ions.

**Figure S6.** The intensity comparison of the emissions at 415 and 620 nm from L1-Eu system along with the reaction.
Figure S7. (a) UV-Vis absorption spectrum of \( \text{L1} \) and (b) phosphorescence spectrum of \( \text{L1-Gd MOF} \) at 77 K.

Figure S8. Fluorescence variation of \( \text{L2-Ln} \) system in DMF with different reaction time. (a) \( \text{L2-Eu} \), (b) \( \text{L2-Tb} \) and (c) \( \text{L2-Gd} \) systems. (d) The enlarged part of \( \text{L2-Eu} \) system to reveal the characteristic luminescence emission of Eu\(^{3+} \) ions. The lowest lines in the figures are the emission from single \( \text{L2} \). After the addition of Ln\(^{3+} \), the fluorescence intensity was measured within 120 min. (e) The emission of \( \text{L2-Gd MOF} \) at room temperature and 77K.
Figure S9. Fluorescence variation of L3-Ln system in DMF with different reaction time. (a) L3-Eu, (b) L3-Tb and (c) L3-Gd systems. (d) The enlarged part from L3-Eu system to reveal the characteristic emission of L3. (e) The enlarged part from L3-Tb system to reveal the characteristic emission variety of L3. The lowest lines in the figures are the emission from single L3.

Figure S10. The pictures of single crystal (a) L1-Eu MOF, (b) L1-Tb MOF, (c) L1-Gd MOF.
**Figure S11.** Fourier transform infrared spectra of L1, L1-Eu MOF, L1-Tb MOF, and L1-Gd MOF.

**Figure S12.** Thermogravimetric analysis of L1, L1-Eu MOF, L1-Tb MOF, and L1-Gd MOF.
Figure S13. (a) Nitrogen adsorption and desorption isotherm of L1-Eu MOF. (b) The corresponding pore size distribution calculated from N$_2$ adsorption isotherms.

Figure S14. The PXRD pattern of L1-Eu MOF before and after being soaked into different solutions for 24 h.
Figure S15. UV-Visible absorption spectra of L1 and L1-Eu MOF.

Figure S16. Fluorescence emission and excitation spectra of L1.
Figure S17. Fluorescence and excitation spectra of **L1-Eu MOF** (excitation spectra in blue for the emission at 415 nm and that in yellow for the emission at 620 nm).

Figure S18. (a) Dual emissions of **L1-Eu MOF** under the excitation from 240 nm to 320 nm with span of 10 nm. (b) 2D mapping of fluorescence spectrum of **L1-Eu MOF**.
Figure S19. The fluorescence lifetime of L1-Eu MOF for emission at 620 nm.

Figure S20. AIE property of L1-Eu MOF in DMF with different water contents. (a) nanosheets, (b) nanospheres.
Figure S21. Fluorescence intensity variation at 415 nm of L1-Eu MOF nanosheets and nanospheres in DMF with different water contents.

Figure S22. Dual-emission enhancement of L1-Eu MOF along with the reduced temperature.
**Figure S23.** PXRD patterns of the as-made L1-Eu MOF before and after being soaked in arginine solution.

**Figure S24.** Time-dependent response of L1-Eu MOF after the addition of arginine.
Figure S25. (a) The fluorescence profiles of L1-Eu MOF at red region with arginine at different concentrations. The intensity decreased gradually. (b) The fluorescence linear fit of $I_1/I_2$ (insert: from left to right: pictures of pure arginine, pure L1-Eu MOF, and their mixture).

Figure S26. 400 nm emission response of L1-Eu MOF to different amino acids. (a) glycine, (b) alanine, (c) leucine, (d) isoleucine, (e) valine, (f) glutamine, (g) cysteine, (h) threonine, (i) phenylalanine, (j) tyrosine, (k) asparagine, (l) serine, (m) methionine, (n) glutamic, (o) histidine, (p) aspartic acid, (q) glutamine, (r) lysine, (s) tryptophan, (t) arginine.
Figure S27. The fluorescence profiles of tryptophan, arginine, and lysine.

Figure S28. TCPB-Eu MOF response to arginine with the arginine content ranged from 0 to 150 μM.
**Figure S29.** Fluorescence profiles of L2-Eu MOF at blue region with arginine content ranged from 0 to 150 μM.

**Figure S30.** (a) L1 response to arginine with different concentrations and (b) concentration-dependent intensity.
**Figure S31.** The UV-Vis spectra of L1, L1-Eu MOF as well as L1 and L1-Eu MOF in the present of arginine.

**Figure S32.** The $^1$H NMR spectra of pure L1, pure arginine, and the mixture of L1 and arginine.
Figure S33. $^1$H NMR spectra of L1 (solvent CDCl$_3$).

Figure S34. $^1$H NMR spectra of L1 (solvent DMSO-D$_6$).
Figure S35. The HPLC chromatogram of L1.

Figure S36. (a) MS spectrum of L1. (b) The enlarged MS spectrum in the red frame of L1.
Table S1 The energy level of Eu$^{3+}$, Tb$^{3+}$ and Gd$^{3+}$ and the energy gap between T1 and excited state of Ln$^{3+}$ ions.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Ln$^{3+}$</th>
<th>Ion energy level (cm$^{-1}$)</th>
<th>$\Delta E_2$ (cm$^{-1}$)</th>
<th>$\Delta E_2'$ (cm$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>L1</td>
<td>Eu$^{3+}$</td>
<td>17500</td>
<td>5919</td>
<td>6596</td>
</tr>
<tr>
<td></td>
<td>Tb$^{3+}$</td>
<td>20500</td>
<td>2864</td>
<td>3596</td>
</tr>
<tr>
<td></td>
<td>Gd$^{3+}$</td>
<td>32500</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>L2</td>
<td>Eu$^{3+}$</td>
<td>17500</td>
<td>2949</td>
<td>3959</td>
</tr>
</tbody>
</table>

$\Delta E_2 / \Delta E_2'$: Energy gap between T1 and Ln ions at before and after the reaction.

Table S2 The synthetic process of the L1-Eu MOF with different apparent structure

<table>
<thead>
<tr>
<th>DMA</th>
<th>DMF</th>
<th>MeOH</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>a*</td>
<td>10</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>b</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>c</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>d#</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>e*</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>f</td>
<td>5</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Note: a-f corresponds to Figure 5 (a)-(f).

*The ratio of Eu$^{3+}$: L1 is 10:1, and the others are 6:1; # reaction in closed glass bottle under 85 °C and the others under 120 °C in stainless steel Teflon-lined autoclave for 3 days. The powder materials are collected by the centrifugation process.

DMA: N, N'-dimethylacetamide, DMF: N, N'-methylformamide, and MeOH: methanol
Supporting References


