## **Electronic Supplementary Information**

# Mechanical grinding of a single-crystalline metal-organic framework triggered emission with tunable violet-to-orange luminescence

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### Section 1. Materials and General Procedures

General information. All chemicals were obtained from commercial sources and of GR/AR grade. FT-IR spectrum (KBr pellets) was recorded on a Bomem MB-102 FT-IR Thermogravimetric (TG) analysis was performed on a Mettler spectrometer. TGA/SDTA851<sup>e</sup> thermal analyzer in flowing air atmosphere at a heating rate of 10 °C·min<sup>-1</sup> from 30 to 1000 °C. Elemental analysis (EA) of C, H and N was performed on a Vario EL III CHNOS elemental analyzer. Powder X-ray diffraction (PXRD) patterns were recorded on MiniFlex diffractometer using graphite-monochromated for Cu K $\alpha$  ( $\lambda$  = 1.5406 Å) radiation in the 20 range of 5-65°. The UV-irradiation experiments were conducted with a 365 nm UV lamp. UV-vis diffuse reflectance spectral measurements were carried out with a Perkin–Elmer Lambda 950 spectrometer. The spectrophotometer was calibrated against the surface of BaSO<sub>4</sub> for 100% reflectance over the wavelength range under consideration. The photoluminescence spectra and quantum yield were determined at room temperature by a FLS920 fluorescence spectrometer. <sup>1</sup>H NMR (400 MHz) spectrum was recorded in a D<sub>2</sub>O solution using a Bruker AVANCE 400 NMR spectrometer.

**Synthesis of H<sub>2</sub>BpebcCl<sub>2</sub>**. The ligand H<sub>2</sub>BpebcCl<sub>2</sub> was synthesized with the following method: A mixture of 1,2-Bis(4-pyridyl)ethylene (1.82 g, 10 mmol) and 4- (chloromethyl)benzoic acid (5.11 g, 30 mmol) was dissolved in 60 mL of DMF and then stirred at 110 °C under nitrogen for 8 h. After the mixture was cooled to room temperature, the resulting red precipitate was collected by filtration, washed with DMF, and dried in a

vacuum to give H<sub>2</sub>BpebcCl<sub>2</sub> as pink powders (yield 65%). IR (KBr, cm<sup>-1</sup>): 3409(s), 3124(m), 1698(s), 1628(s), 1517(m), 1467(m), 1399(s), 1228(w), 1209(w), 1160(m), 1111(m), 987(m), 846(w), 751(m), 555(m), 477(w). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  8.96 (d, J = 6.8 Hz, 4H), 8.30 (d, J = 6.8 Hz, 4H), 8.13 (d, J = 8.3 Hz, 4H), 7.93 (s, 2H), 7.61 (d, J = 8.3 Hz, 4H), 5.94 (s, 4H).



Scheme S1 Schematic representation of the synthesis procedure of H<sub>2</sub>BpebcCl<sub>2</sub>.

**Synthesis of {**[**Eu(Bpebc)**<sub>1.5</sub>(**SO**<sub>4</sub>)(**H**<sub>2</sub>**O**)<sub>2</sub>]·(**OH**)·16.5**H**<sub>2</sub>**O**}<sub>n</sub> 1: H<sub>2</sub>BpebcCl<sub>2</sub> (26.1 mg, 0.05 mmol) was dissolved in 5 mL of water, and the pH value of the solution was adjusted to 7 with 0.1 mol·L<sup>-1</sup> NaOH solution. An aqueous solution of Eu<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O, (0.05 mmol in 2 mL of water) was then added to the above reaction mixture. After the mixture was stirred for 5 min, the residue was filtered. The filtrate was allowed to stand for several days to give red crystals (Yield: 40%). The obtained crystals were further washed by distilled water and ethanol for several times and dried at room temperature. EA Calcd. (%) for C<sub>42</sub>H<sub>71</sub>EuN<sub>3</sub>O<sub>29.5</sub>S (*M*r = 1274.04): C, 39.59; H, 5.61; N, 3.30. Found (%): C, 39.76; H, 5.39; N, 3.22. The EA for ground sample **g-1**: C, 39.75; H, 5.38; N, 3.44.

The guest-inclusion experiments were performed by immersion of g-1 (20 mg) into an aqueous solution (6 mL) of phloroglucinol (10 mg) and trinitrophenol (10 mg), respectively, for two days. As for the encapsulation of the nitrobenzene, the g-1 (20 mg) sample was directly immersed in 6 mL of nitrobenzene solution. The resulting materials were carefully washed by distilled water and ethanol and then dried at room temperature. The amount of adsorbed aromatic molecules was evaluated by EA. EA Calcd (%) for g-1

⇒ phloroglucinol, {[Eu(Bpebc)<sub>1.5</sub>(SO<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>]·(OH)·7.5H<sub>2</sub>O·2(C<sub>6</sub>O<sub>3</sub>H<sub>6</sub>)}<sub>n</sub>: C, 47.55; H, 4.80; N, 3.08; found (%) **g-1** ⇒ phloroglucinol: C, 47.39; H, 5.12; N, 3.30. Calcd (%) for **g-1** ⇒ trinitrophenol, {[Eu(Bpebc)<sub>1.5</sub>(SO<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>]·(OH)·2H<sub>2</sub>O·2(C<sub>6</sub>O<sub>7</sub>N<sub>3</sub>H<sub>3</sub>)}<sub>n</sub> C, 44.09; H,3.29; N, 8.57; found (%) for **g-1** ⇒ trinitrophenol: C, 43.95; H, 3.45; N, 8.97. Calcd (%) for **g-1** ⇒ nitrobenzene, {[Eu(Bpebc)<sub>1.5</sub>(SO<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>]·(OH)·11H<sub>2</sub>O·0.5(C<sub>6</sub>O<sub>2</sub>NH<sub>5</sub>)}<sub>n</sub> C, 43.71; H, 5.09; N, 3.96; found (%) **g-1** ⇒ nitrobenzene: C, 43.45; H, 4.52, N, 3.59.

**X-ray crystallography.** The X-ray diffraction data for **1** was collected on Agilent Xcalibur Atlas Gemini ultra diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 107 K. Adsorption correction was performed by multi-scan method. The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares fitting on F<sup>2</sup> by SHELXL-97.<sup>1</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of ligands were calculated in ideal positions with isotropic displacement parameters. The guest anions were highly disordered and the "squeeze" protocol was used to subtract the diffraction contribution from the solvent molecules and then the structure was refined further by using the data generated.<sup>2</sup> The proposed formula of **1** was estimated by the EA and thermal gravimetric analysis.

Crystal data for 1: C<sub>42</sub>H<sub>71</sub>EuN<sub>3</sub>O<sub>29.5</sub>S,  $M_r = 1274.04$ , space group *R*-3; a = 17.6479(13), b = 17.6479(13), c = 31.002(2) Å;  $\alpha = 90$ ,  $\beta = 90$ ,  $\gamma = 120^{\circ}$ ; T = 107 K, Z = 6, V = 8361.9(10) Å<sup>3</sup>,  $D_c = 1.518$  g cm<sup>-3</sup>,  $\mu = 1.254$  mm<sup>-1</sup>, F(000) = 3954 and GOF = 1.090. 11017 reflections collected, 3270 unique ( $R_{int} = 0.0828$ ).  $R_1 = 0.0981$ , w $R_2 = 0.2244$  [ $I > 2\sigma(I$ ]]. CCDC 993232

**Computation description.** The charge Mulliken population calculations were carried out by using Dmol3 program,<sup>3</sup> where the GGA calculations were performed by PBE exchange correlation. In order to save the computational effort and ignore the magnetism of 4f electrons of Eu(III) during calculation, the Eu(III) were substituted by diamagnetic lanthanide Y(III) owing to its similar ion radii and electronegativity. Mulliken charges

were calculated by projecting the occupied one-electron eigenstates onto the localized atomic basis sets.<sup>4</sup>

#### References

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#### Section 2. Additional Data and Pictures



Fig. S1 The overall n-Borromean entanglement of the infinite layers  $(2D \rightarrow 3D)$  in 1.



**Fig. S2** Left: The emission spectra of H<sub>2</sub>BpebcCl<sub>2</sub> in aqueous solution (10<sup>-3</sup> M). Middle: Photograph showing the white light emission of H<sub>2</sub>BpebcCl<sub>2</sub> solution under 365 nm UV light. Right: the excitation spectrum ( $\lambda_{em} = 637$  nm) of H<sub>2</sub>BpebcCl<sub>2</sub> in aqueous solution (10<sup>-3</sup> M).



**Fig. S3** The black dots signify the color coordinates for the emissions of the H<sub>2</sub>BpebcCl<sub>2</sub> in aqueous solution, a (0.35, 0.37),  $\lambda_{ex} = 380$  nm, b (0.61, 0.38),  $\lambda_{ex} = 505$  nm.



**Fig. S4** The visual color changes of ground sample **g-1** (a) after encapsulation of electron-donating guest molecules (b) phloroglucinol and (d) trinitrophenol. No color change is observed after encapsulation of electron-withdrawing guest (f) nitrobenzene. The corresponding luminescence changes are detected under 365 nm light. Further grindings of the samples (c and e) can not turn on the luminescence.



**Fig. S5** The UV-Vis diffuse reflectance spectral changes of **g-1** after encapsulation of different guests. The original **g-1**(black), after encapsulation of trinitrophenol (red), after encapsulation of phloroglucinol (green).



**Fig. S6** TOP: PXRD records for (a) calculated pattern from 1, (b) as-synthesized single crystal 1, (c) ground sample **g-1**, (d) recrystallized single crystal. The PXRD patterns in right panel show the shifts of the (2-10), (2-13), (3-1-2) and (300) peaks after grinding single crystals. Bottom: suggested relative shift between adjacent benzoic and pyridinium moieties after an external pressure stimulus (Eu: green, O: red, C: gray, N: blue).



Fig. S7 The change in the emission spectra before (red) and after (black) grinding single crystal 1 ( $\lambda_{ex} = 380 \text{ nm}$ ).



Fig. S8 The TG plot of 1.



Fig. S10  $^{1}$ H NMR (400 MHz, D<sub>2</sub>O) for H<sub>2</sub>BpebcCl<sub>2</sub>.

Table S1. Selected Charges from the DFT Analysis

Groups	Pyridinium ring	Carboxylate group
Atom label	From N1 to C13	O5-C1-O6
Total Charge	+0.37	-0.59