Supporting Information

# A novel luminescence phosphor of metal-organic framework with orange-red emission

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## 2. Experimental section

### 1. Synthesis:

A suspension of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 mmol, 0.34 g), 4,4'-((1E,1'E)-(2,5-dibutoxy-1,4-phenylene)bis(ethene-2,1-diyl))dipyridine (abbreviated as DPBD, 0.01 mmol, 0.043g) and 2,5-dichloroterephthalic acid (abbreviated as $H_2$DBTT, 0.01 mmol, 0.047g) in 3 mL of DMF/$H_2O$ (3:1, v/v) and a drop of HCl (2 mol/L) was sealed in a 10 mL Teflon-lined stainless steel autoclave and heated under autogenous pressure at 100°C for 72 h. After the autoclave was cooled to room temperature, orange block single crystals suitable for single-crystal X-ray crystallographic analysis were obtained. The resulting crystals were rinsed three times with DMF and dried at room temperature overnight for further characterization. Yield: 14.1 mg (13.2% based on DPBD). The phase purity was confirmed by powder X-ray diffraction (Figure S1 in Supporting Information).

### 2. Characterization

Thermogravimetric analysis (TGA) was checked on a Perkin-Elmer thermal analyzer under nitrogen with a heating rate of 10°C/min. Powder X-ray diffraction (PXRD) patterns were carried out on a Bruker D8 Advance instrument using Cu Kα radiation at room temperature (2θ = 5–50°, 0.1 s/deg). The photoluminescent spectra was executed on an Agilent Cary Eclipse Fluorescence spectrophotometer.

## 3. Crystallographic Data

A suitable single crystal of compound **1** was selected to carry out single-crystal X-ray diffraction data by a Bruker D8 venture diffractometer, using a photon CMOS-detector and graphite-monochromated Mo-Ka radiation (0.71073 Å) at room temperature. After collection, the data reduction and absorption correction were executed by the SAINT [1] and SADABS [2] subprograms of APEX3 [3] software package, respectively. Then, the structures were solved by dual space method using SHELXT [4] routine, and further refined by SHELXL [5] subprogram by full-matrix least squares on $F^2$ under Olex2 [6] program. All the hydrogen atoms were resided at their ideal geometric positions by theoretical calculation and refined isotropically using a riding model, and all non-hydrogen atoms were refined anisotropically. Summary of structural parameters and crystal data of compound **1** were given in Tables S1 to S3. Crystallographic data were deposited in the Cambridge Crystallographic Data Centre (CCDC No. 2114789).

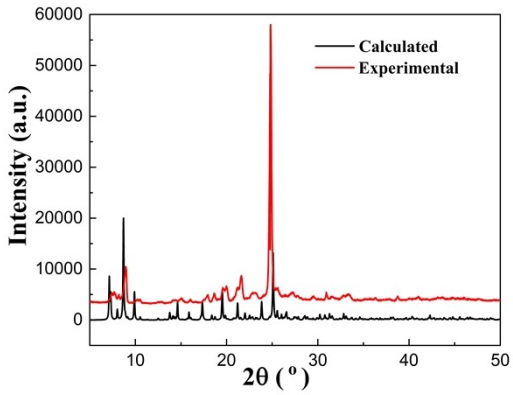


**Figure S1.** Powder X-ray diffraction (PXRD) patterns of compound **1**.

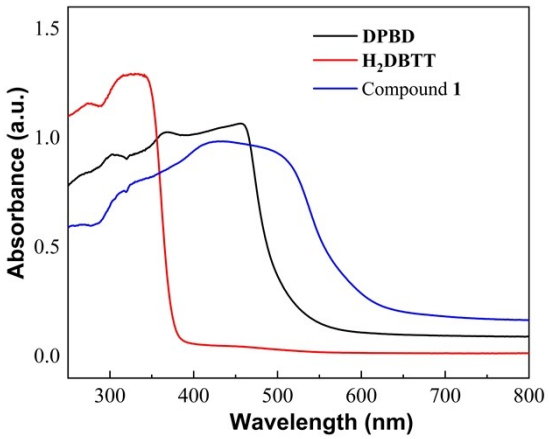


**Figure S2.** The UV-vis diffuse reflection spectra of compound **1** and free ligands of $H_2$DBTT and DPBD.

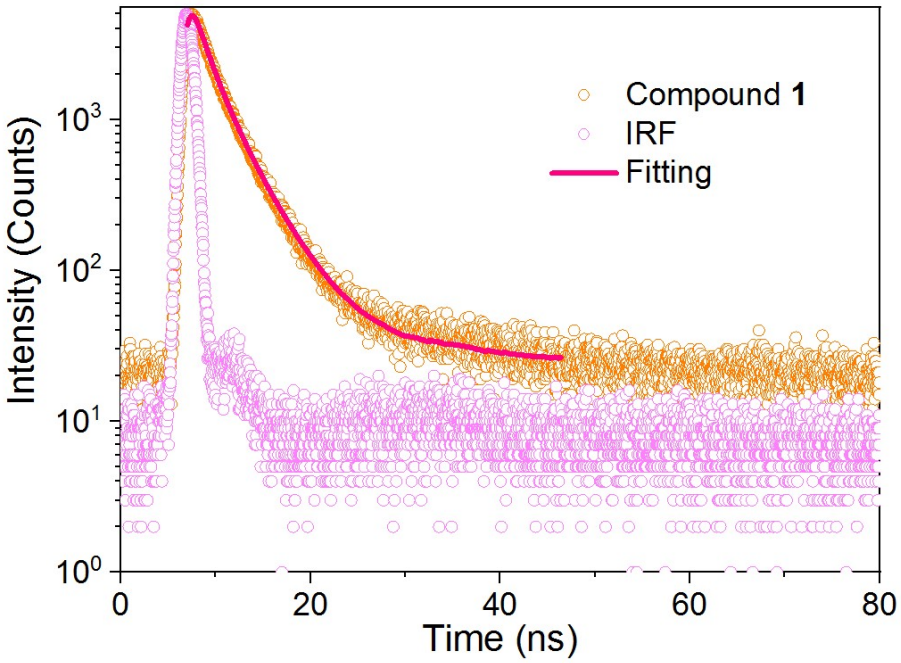


**Figure S3.** Fluorescence lifetimes of compound **1** derived from a least-square fit using double exponential function with internal reference.

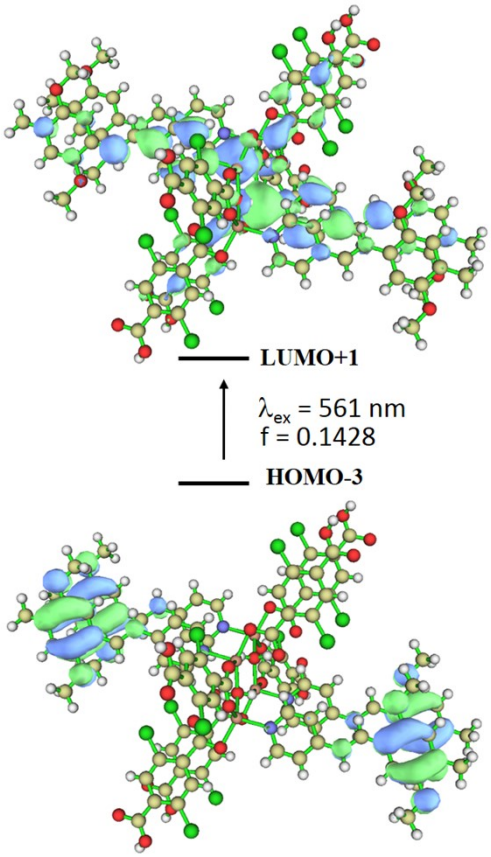


**Figure S4.** The calculated molecular orbitals of compound **1** drawn by Multiwfn [7, 8] programs.

Table S1. Crystal data and structure refinement for compound **1**:.

| | | |
|---|---|---|
| Empirical formula | $C_{78.20}\ H_{71.55}\ Cl_{5.55}\ N_{4.45}\ O_{18.45}\ Zn_4$ | |
| Formula weight | 1827.15 | |
| Temperature | 153.15 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a = 12.662(2) Å | α= 90.626(3)°. |
| | b = 13.459(2) Å | β= 96.747(3)°. |
| | c = 24.432(4) Å | γ = 112.981(3)°. |
| Volume | 3799.3(10) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.597 $Mg/m^3$ | |
| Absorption coefficient | 1.518 $mm^{-1}$ | |
| F(000) | 1868 | |
| Crystal size | 0.15 x 0.14 x 0.11 $mm^3$ | |
| Theta range for data collection | 1.647 to 26.433°. | |
| Index ranges | -12<=h<=15, -16<=k<=16, -30<=l<=30 | |
| Reflections collected | 21198 | |
| Independent reflections | 15215 [R(int) = 0.0388] | |
| Completeness to theta = 25.242° | 98.0 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7454 and 0.6057 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 15215 / 650 / 1101 | |
| Goodness-of-fit on $F^2$ | 0.927 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0615, wR2 = 0.1445 | |
| R indices (all data) | R1 = 0.1267, wR2 = 0.1746 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 1.367 and -0.752 $e.Å^{-3}$ | |

Table S2. Bond lengths [Å] and angles [°] for compound **1**:.

| | |
|---|---|
| Zn(1)-O(2) | 1.927(3) |
| Zn(1)-O(3) | 1.986(5) |
| Zn(1)-O(5) | 1.983(4) |
| Zn(1)-O(19) | 2.53(2) |
| Zn(1)-O(23) | 1.989(10) |
| Zn(1)-N(4) | 2.015(4) |
| Zn(2)-O(2) | 1.992(3) |
| Zn(2)-O(2)#1 | 2.275(3) |
| Zn(2)-O(13)#2 | 2.065(4) |
| Zn(2)-O(14) | 2.141(5) |
| Zn(2)-O(16)#2 | 2.326(4) |
| Zn(2)-O(24) | 2.042(10) |
| Zn(2)-N(1)#3 | 2.095(4) |
| Zn(3)-O(1) | 1.978(3) |
| Zn(3)-O(1)#4 | 2.369(4) |
| Zn(3)-O(7) | 2.014(4) |
| Zn(3)-O(9) | 2.513(4) |
| Zn(3)-O(18) | 2.100(5) |
| Zn(3)-O(22) | 2.024(9) |
| Zn(3)-N(3)#5 | 2.058(4) |
| Zn(4)-O(1) | 1.930(3) |
| Zn(4)-O(6) | 1.997(5) |
| Zn(4)-O(8) | 1.964(4) |
| Zn(4)-O(15) | 2.580(4) |
| Zn(4)-O(21) | 2.005(9) |
| Zn(4)-N(2) | 2.019(5) |
| O(2)-Zn(1)-O(3) | 115.8(2) |
| O(2)-Zn(1)-O(5) | 113.98(16) |
| O(2)-Zn(1)-O(19) | 83.2(4) |
| O(2)-Zn(1)-O(23) | 108.5(10) |
| O(2)-Zn(1)-N(4) | 109.33(16) |
| O(5)-Zn(1)-O(3) | 107.9(3) |
| O(5)-Zn(1)-O(19) | 54.1(3) |
| O(5)-Zn(1)-O(23) | 114.8(14) |
| O(5)-Zn(1)-N(4) | 105.20(17) |
| O(2)-Zn(2)-O(2)#1 | 77.59(13) |
| O(2)-Zn(2)-O(13)#2 | 153.63(16) |

| | |
|---|---|
| O(2)-Zn(2)-O(14) | 95.3(3) |
| O(2)#1-Zn(2)-O(16)#2 | 79.19(15) |
| O(2)-Zn(2)-O(16)#2 | 96.43(15) |
| O(2)-Zn(2)-O(24) | 94.8(13) |
| O(2)-Zn(2)-N(1)#3 | 106.84(16) |
| O(1)-Zn(3)-O(1)#4 | 77.49(13) |
| O(1)-Zn(3)-O(7) | 152.86(16) |
| O(1)#4-Zn(3)-O(9) | 70.72(13) |
| O(1)-Zn(3)-O(9) | 97.27(13) |
| O(1)-Zn(3)-O(18) | 97.7(3) |
| O(1)-Zn(3)-O(22) | 94.1(8) |
| O(1)-Zn(3)-N(3)#5 | 103.53(17) |
| O(1)-Zn(4)-O(6) | 111.1(3) |
| O(1)-Zn(4)-O(8) | 124.10(16) |
| O(1)-Zn(4)-O(15) | 85.34(14) |
| O(1)-Zn(4)-O(21) | 108.2(8) |
| O(1)-Zn(4)-N(2) | 103.92(16) |

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1 #2 x+1,y,z+1 #3 x+1,y-1,z

#4 -x+1,-y+1,-z #5 x,y-1,z-1 #6 -x+1,-y,-z+1

#7 -x,-y,-z #8 x-1,y,z-1 #9 x-1,y+1,z #10 x,y+1,z+1

Table S3. Hydrogen bonds for compound **1**: [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| C(1)-H(1A)...O(7)#10 | 0.95 | 2.56 | 3.168(7) | 122.0 |
| C(5)-H(5)...O(15)#10 | 0.95 | 2.49 | 3.346(7) | 149.7 |
| C(22)-H(22)...O(16)#2 | 0.95 | 2.49 | 3.416(7) | 163.5 |
| C(49)-H(49)...O(9) | 0.95 | 2.48 | 3.397(6) | 163.6 |
| C(54)-H(54)...O(6)#11 | 0.95 | 2.43 | 3.311(10) | 153.9 |
| C(70)-H(70)...O(13)#10 | 0.95 | 2.48 | 3.110(7) | 123.8 |
| C(71)-H(71)...O(17)#9 | 0.95 | 2.33 | 3.253(8) | 164.2 |
| C(71)-H(71)...O(19)#9 | 0.95 | 2.58 | 3.417(15) | 147.4 |

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1 #2 x+1,y,z+1 #3 x+1,y-1,z

#4 -x+1,-y+1,-z #5 x,y-1,z-1 #6 -x+1,-y,-z+1

#7 -x,-y,-z #8 x-1,y,z-1 #9 x-1,y+1,z #10 x,y+1,z+1

#11 -x,-y+1,-z

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