Supporting Information

A luminescent turn-up metal-organic framework sensor for tryptophan based on singlet-singlet Förster energy transfer

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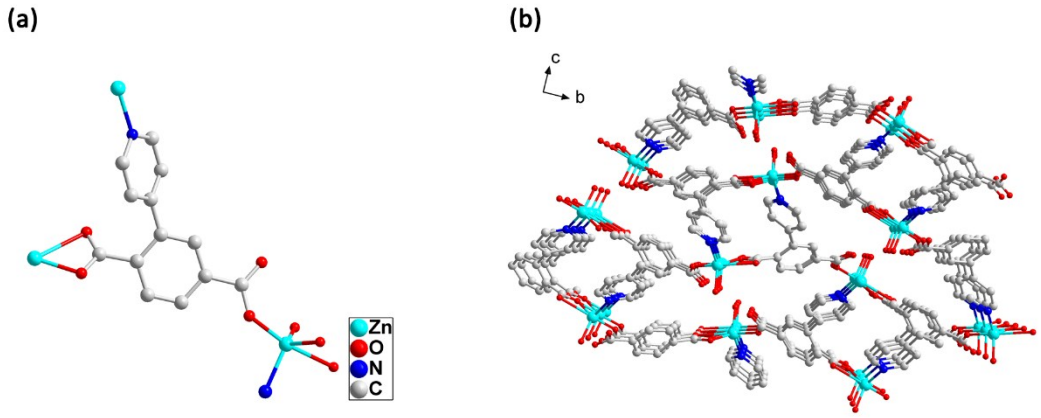

Figure S1. (a) The coordination environments of H_2pta ligand; (b) The 3D packing structure of **ZJU-108** along the *a*-axis. The hydrogen atoms are omitted for clarity.

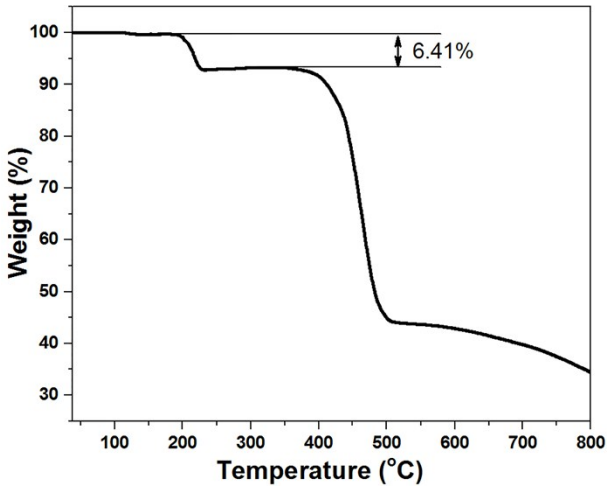

Figure S2. TGA curves of **ZJU-108.**

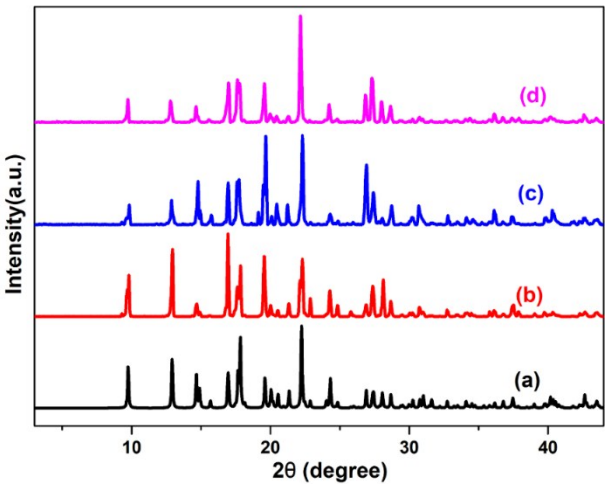

Figure S3. The PXRD patterns of (a)sim-**ZJU-108**; (b)syn-**ZJU-108**; (c)**ZJU-108** in H_2O for one month; (d)**ZJU-108** in tryptophan aqueous solution (0.1 mM) for 3 days.

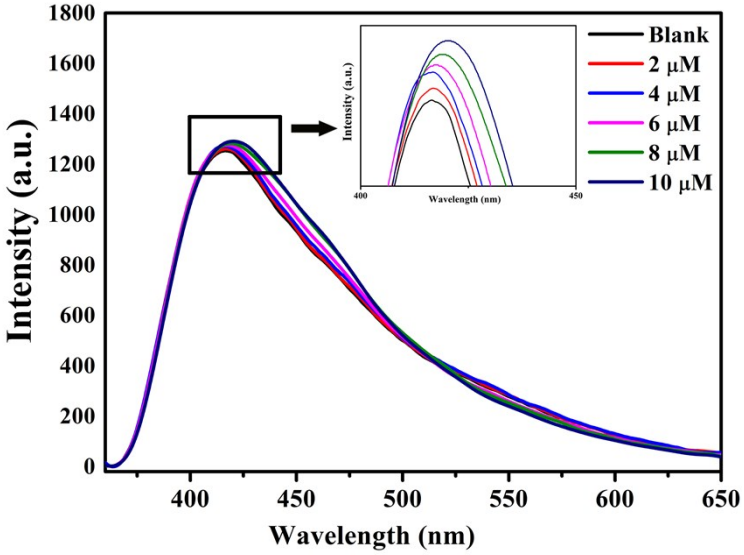

Figure S4. Luminescence response of ZJU-108 to different concentration (0-10 μM) of tryptophan in aqueous solution.

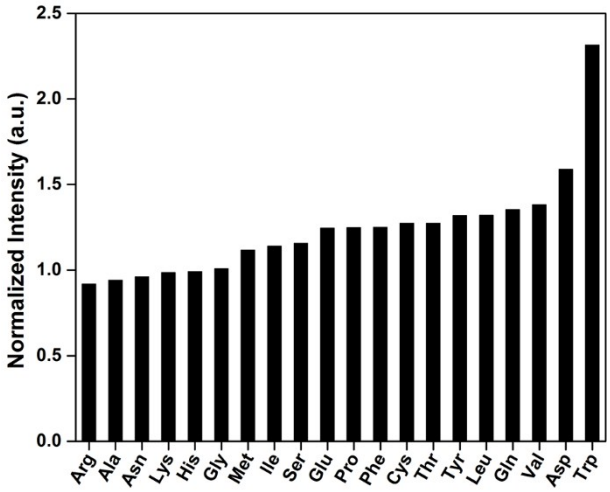

Figure S5. Luminescence response of **ZJU-108** to different amino acids (0.5 mM) in aqueous solution. The excitation wavelength is 323 nm.

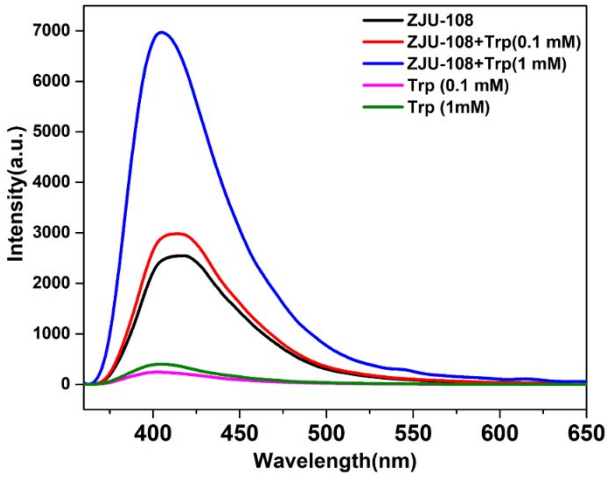

Figure S6. The emission spectra of **ZJU-108**, Trp and **ZJU-108**-Trp under the same experiment conditions. The excitation wavelength is 323 nm.

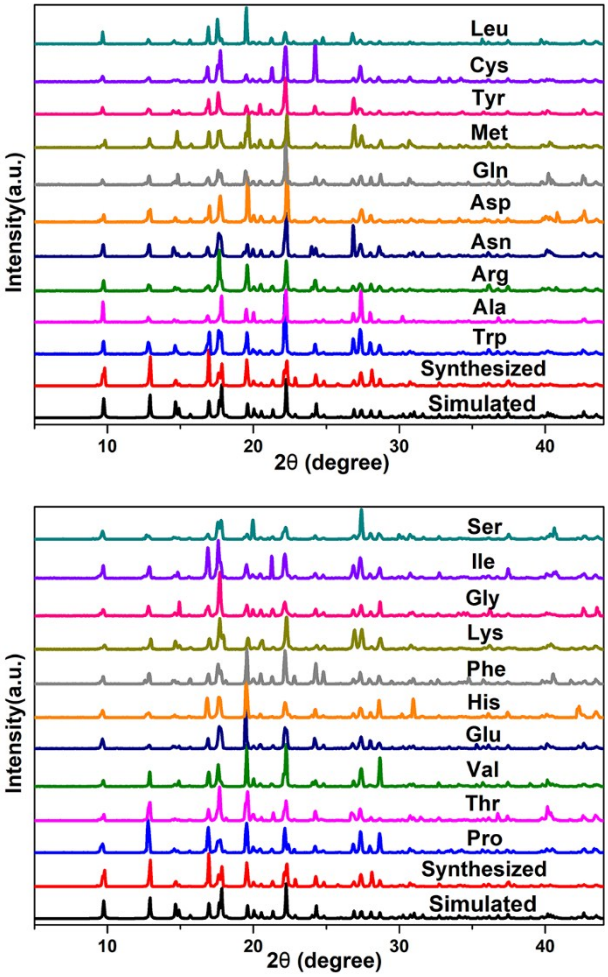

Figure S7. The PXRD patterns of **ZJU-108** in aqueous solutions of different amino acids (0.1 mM) for 3 days.

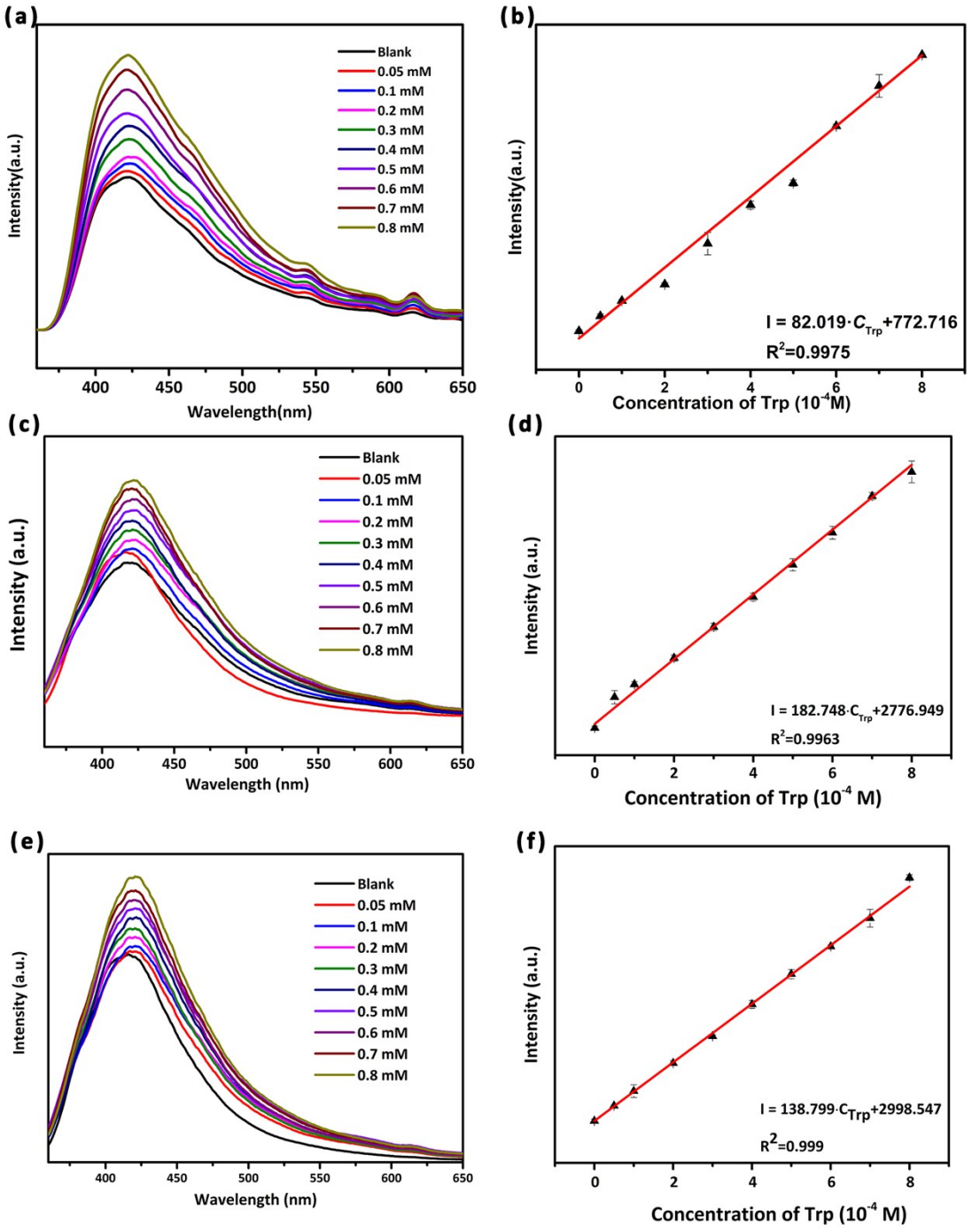

Figure S8. (a) Luminescence response of **ZJU-108** to different concentrations of tryptophan in serum; (b) Concentration dependence of the luminescence intensity at 419 nm in serum. (c) Luminescence response of **ZJU-108** to different concentrations of tryptophan in urine; (d) Concentration dependence of the luminescence intensity at 419 nm in urine. (e) Luminescence response of **ZJU-108** to different concentrations of tryptophan in intracellular fluid; (f) Concentration dependence of the luminescence intensity at 419 nm intracellular fluid. All luminescence experiments were tested in triplicate and the excitation wavelength is 323 nm.

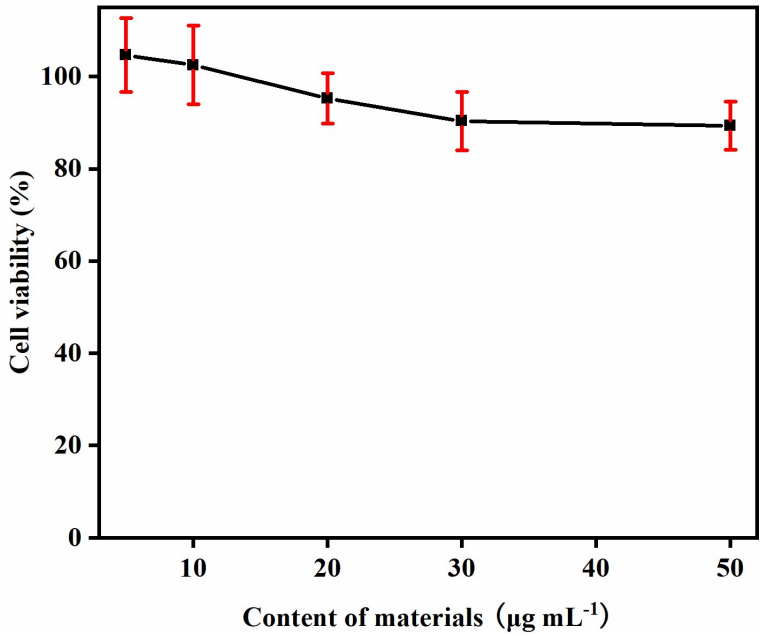

Figure S9. MTT assay of **ZJU-108** obtained from incubation with PC12 Cells

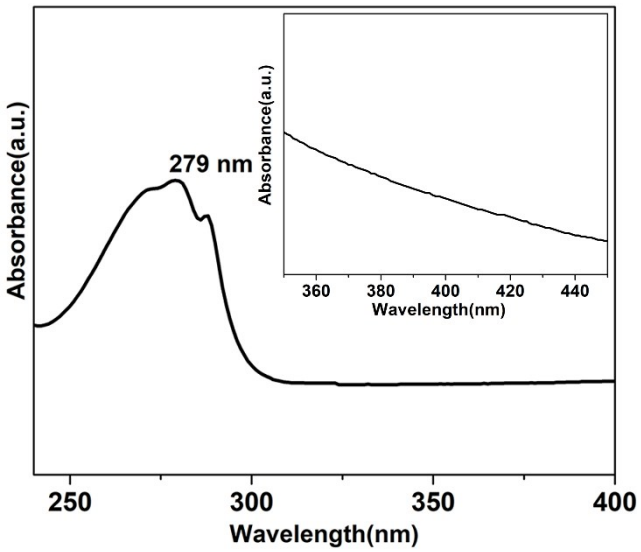

Figure S10. The UV-vis absorption spectrum for Trp, inset: Enlarged spectrum between 350 nm to 450 nm.

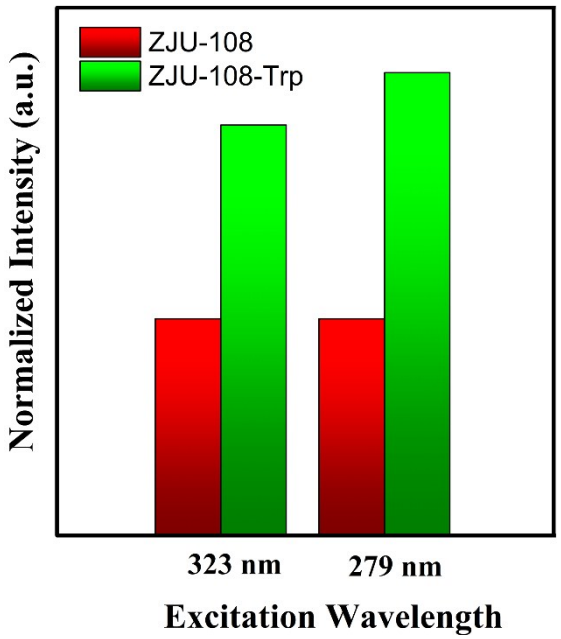

Figure S11. The normalized emission intensity of **ZJU-108** and **ZJU-108**-Trp upon the excitation of 323 and 279 nm.

Table S1. Crystallographic data collection and refinement details for **ZJU-108**.

ZJU-108	
Empirical formula	$C_{13}H_8NO_5Zn$
Formula weight	323.57
Temperature/K	293(2)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	P2(1)/n
a/Å	6.4995(2)
b/Å	18.1405(5)
c/Å	10.6050(3)
α/°	90
β/°	100.155(2)
γ/°	90
Z	4
Density (calculated g cm-3)	1.7461
Absorption coefficient/ mm-1	2.012
Reflections collected	25915
Independent reflections	2146 [R(int) = 0.0237]
F(000)	652
Goodness of fit on F2	1.212
R1,wR2(I>2σ(I))a	0.0359, 0.1340
R1,wR2(all date)a	0.0412, 0.1387
aR1=Σ(|Fo|-|Fc|)/Σ|Fo|; wR2=[Σw(|Fo|-|Fc|2)/ΣwFo2]1/2.	

The structure was determined by direct methods, and refined by the full-matrix least-square method with the SHELX-2013 program package. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. All non-hydrogen atoms were refined with anisotropic thermal parameters, and all H atoms on C atoms were generated geometrically and refined with isotropic thermal parameters.

Table S2. The ICP data for Zn2+ ions in different samples.

Samples	Concentration of Zn^{2+} ion (ppm)
ZJU-108-H_2O	2.76
ZJU-108-pH1.8	35.94
ZJU-108-pH3.1	9.25
ZJU-108-pH6.5	7.64
ZJU-108-pH9.4	6.39
ZJU-108-pH11.7	4.04

The **ZJU-108**-H_2O was obtained by immersing **ZJU-108** in water for 12 hours and tested the amount of Zn^{2+} ions in the soaking solution. Same tests go for the samples of **ZJU-108** in aqueous solution with pH=1.8-11.7.

Table S3. Calculation results of singlet state energy level and the corresponding wavelength of excitation light of H_2pta and selected amino acids.

Amino acids	Singlet state energy level (eV)	Excitation light wavelength (nm)
H_2pta	**3.8009**	**326.20**
Alanine	5.2382	236.69
Arginine	5.2456	236.36
Asparagine	5.1484	240.82
Aspartic Acid	5.2749	235.04
Cysteine	5.1767	239.50
Glutamine	5.3442	232.00
Glutamic Acid	5.3536	231.59
Glycine	5.4098	229.19
Histidine	4.6439	266.98
Isoleucine	5.3979	229.69
Leucine	5.2784	234.89
Lysine	5.4104	229.16
Methionine	5.3779	230.54
Phenylalanine	4.9072	252.66
Proline	5.1332	241.54
Serine	5.2474	236.28
Threonine	5.2171	237.65
L-Tryptophan	**4.3051**	**287.99**
D-Tryptophan	4.3527	284.84
Tyrosine	4.8780	254.17
Valine	5.3902	230.02

The calculation of the amino acids and the ligand were performed using the Gaussian 09 program. All the structures were completely optimized to the ground state by the DFT method at B3LYP/6+g(d,p) level. Then the singlet and triplet energy of structures were calculated based on TD-SCF method.