Zr-MOF Nanoflower Sensor and Its Mixed-Matrix Membrane for Highly Sensitive Nitroaromatics Detection

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1. Experimental Details

1.1. Materials and general methods

All chemicals were obtained through commercial channels and used without further processing and purification. The Power X-ray diffraction data of CJLU-1 were collected on a Bruker D8 Advanced diffractometer with a graphite-monochromatized Cu Kα radiation which was operated at 40 kV and 40 mA. Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FE-SEM) images were obtained by JEM-2100 and Vltra55, Carl Zeiss, respectively. The PL spectrum were obtained by F4600 fluorescence spectrometer. The fluorescence lifetime was carried out on a Fluorolog HORIBA JOBIN YVON. Thermogravimetric analysis (TGA) was taken on TA Instruments Q500 Thermogravimetric Analyzer under N_2 atmosphere at a heating rate of 10 °C/min up to 800 °C. FT-IR was carried out on a Perkin Elmer FTIR SpectrumGX spectrometer. UV-Vis absorption spectrum was recorded on Hitachi U-3900 spectrometer.

1.2. Synthesis of CJLU-1

4,4',4''-nitrilotribenzoicacid (H_3TCA) (94.25 mg, 0.250 mmol) and $ZrCl_4$ (0.0863 g, 0.370 mmol) were added to 10 mL of DMF in 50 mL Teflon-lined stainless-steel autoclave, after the mixture was dissolved, and then add concentrated HCl (10.75 mL, 100 equiv.) to the above mixture. After sonication for 10 minutes, the mixture was heated at 120 ^oC for 2 days. Then, the temperature of the mixture dropped to room temperature and washed by DMF and methanol several times, respectively. And then, the white powder was obtained. **CCDC number is 2164807**.

1.3. Organic small molecule sensing

For organic small molecule sensing experiment, 10 mg sample powder was added to 100 mL ethanol and sonicated for 20 minutes to obtain suspension of CJLU-1. The luminescent sensing experiment was carried out by adding 50 μL of DMF, acetone, phenol, H_2O, aniline, toluene, NB, 2,4-DNT, 2,6-DNT, PNP (p-nitrophenol) and 1.22% PA (among them, the concentration

of 1.22% PA was 5.32×10^{-2} M) with a concentration of 0.1 M to 2 mL suspension of CJLU-1, respectively, and then measuring the PL spectrum.

1.4. Synthesis of CJLU-1 MMMs

200 mg of cellulose acetate was added to 1.8 g of acetone/DMF (mass/mass = 2/1), and sonication was carried out for 5 hours to dissolve the cellulose acetate to obtain casting solution. And then 120 mg of CJLU-1 was added to the above casting solution to form a homogeneous solution by sonication. Then, the casting solution with CJLU-1 was cast onto a glass plate by a wiper and immersed in deionized water to separate the composite membrane from the glass plate. After drying at room temperature, white CJLU-1 MMMs was obtained.

1.5. Fluorescent photo of CJLU-1 MMMs

1×1 cm^2 was cut from CJLU-1 MMMs and it was taken as a simple sensor, and 5 μL of the nitroaromatics was pipetted onto the composite membrane by using a pipetting gun. Under the irradiation of 365 nm ultraviolet lamp, it can be judged by directly observing whether the CJLU-1 MMMs is quenched by naked eyes.

1.6. Gas phase sensing measurements of CJLU-1 MMMs

2 mL of analytes (analytes include nitrobenzene, 2-nitrotoluene and PNP, among them, PNP was solid state, so it was prepared as a 0.1 M ethanol solution) were placed in a 20 mL sample vial, which was placed in a closed reagent bottle and allowed to stand for a few days to bring analytes to equilibrium vapor pressure, respectively. Then 1×1 cm^2 CJLU-1 MMMs was adhered to glass slide by double-sided adhesive. Before it was exposed to the vapor, collect its original emission spectrum. And then placed it into the above reagent bottle to expose it to vapor of analyte. After a certain period of time, the slide was removed from the reagent bottle and its emission spectrum was collected immediately.

1.7 PA sensing measurements of CJLU-1 MMMs

At first, 1×1 cm^2 CJLU-1 MMMs was adhered to glass slide by double-sided adhesive and collect its original emission spectrum. Then transferring 50 μL different concentrations of PA

solution onto MMMs with a pipette, respectively. The analyte solution infiltrates the MMMs and immediately collects their emission spectrums.

1.8 Repeatability test of CJLU-1 MMMs detect vapor of nitrobenzene

First, the emission spectrums of CJLU-1 MMMs before and after exposure for 5 min to vapor of nitrobenzene were collected, respectively. The completely quenched CJLU-1 MMMs was immersed into ethanol for 5 minutes and then dried at room temperature, the fluorescence intensity of CJLU-1 MMMs could be recovered.

2. Structural information

Table S1. Atomic coordinates and refined unit cell parameters of **CJLU-1**.

Name	**CJLU-1**		
Space group	P-3		
a (Å)	17.1940		
b (Å)	17.1940		
c (Å)	7.0100		
Unit Cell Volume	1794.74		
Atom name	x	y	z
C1	0.6801	0.46598	0.92158
C2	0.72926	0.55714	0.96339
C3	0.78829	0.48518	0.67741
C4	0.8378	0.57658	0.71951
C5	0.80943	0.61291	0.86534
C6	0.70996	0.42908	0.78022
C7	0.86332	0.70824	0.91652
O2	0.93997	0.75629	0.83535
H1	0.62076	0.42359	0.00536
H2	0.70566	0.58334	0.07606
H3	0.81221	0.4574	0.56876
H4	0.89894	0.61833	0.64025

H6	0.94552	0.7495	0.24958
H7	0.79692	0.77771	0.45732
H8	0.88182	0.86872	0.52399
O1	0.83127	0.74102	0.03891
O3	0.89212	0.86587	0.86496
O4	0.8948	0.75747	0.29214
O5	0.83427	0.84285	0.42819
Zr1	0.89679	0.87076	0.15934
O6	0.00000	0.00000	0.28367
N1	0.33333	0.66667	0.243

3. Figures

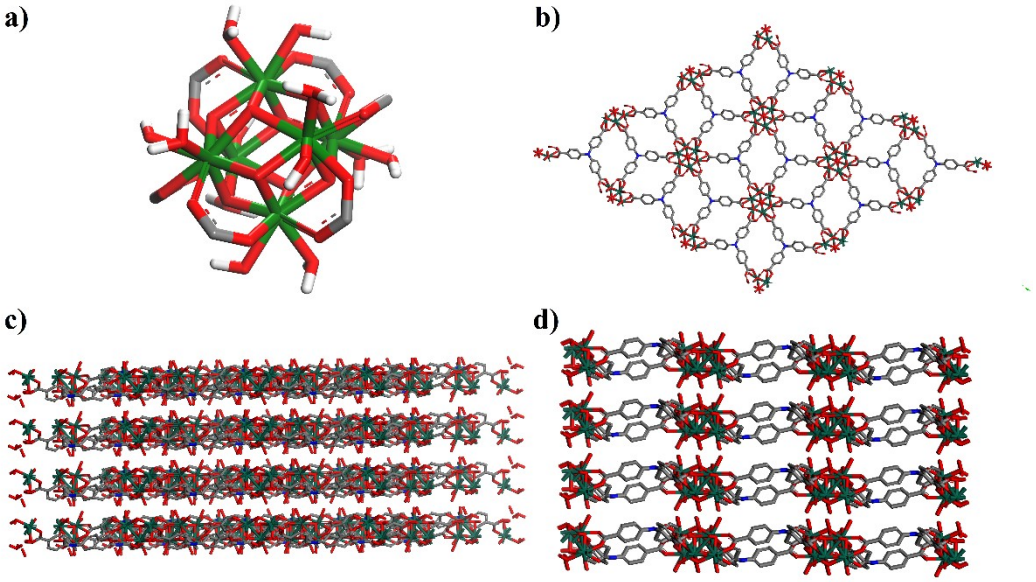


Figure S1. a) The hexagonal $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(OH)_6$ SBU of CJLU-1 b) c) d) Structure of CJLU-1 along z,x and y axis, respectively (green: Zr atom; red: O atom; blue: N atom; grey: C atom) .

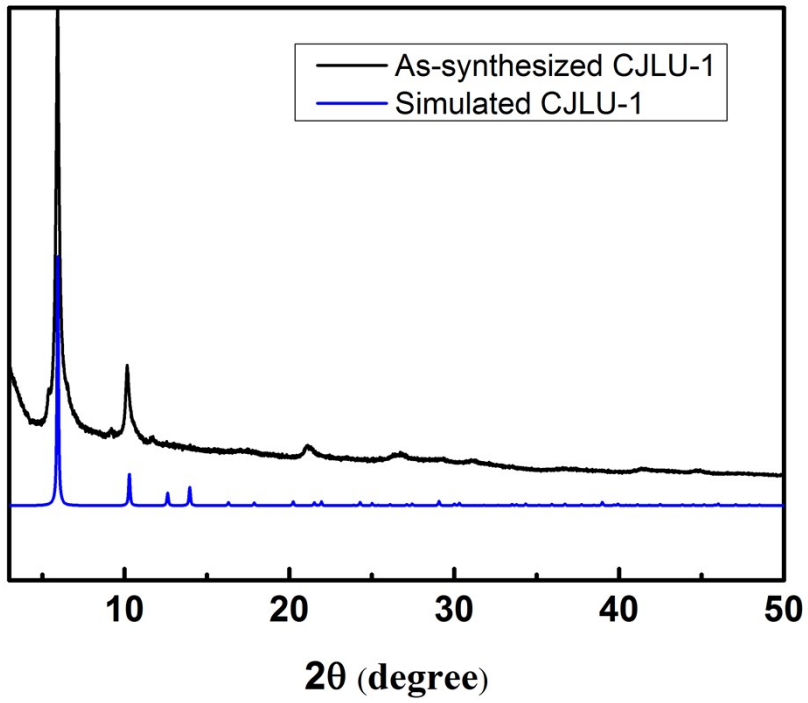


Figure S2. PXRD of simulated and as-synthesized CJLU-1.

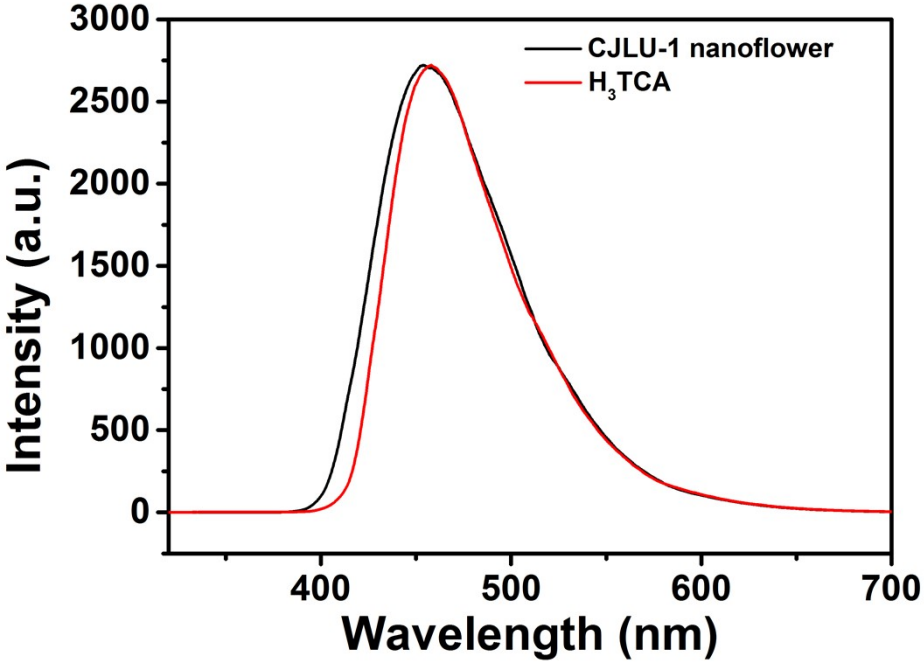


Figure S3. Solid-based PL spectrums of CJLU-1 and H_3TCA.

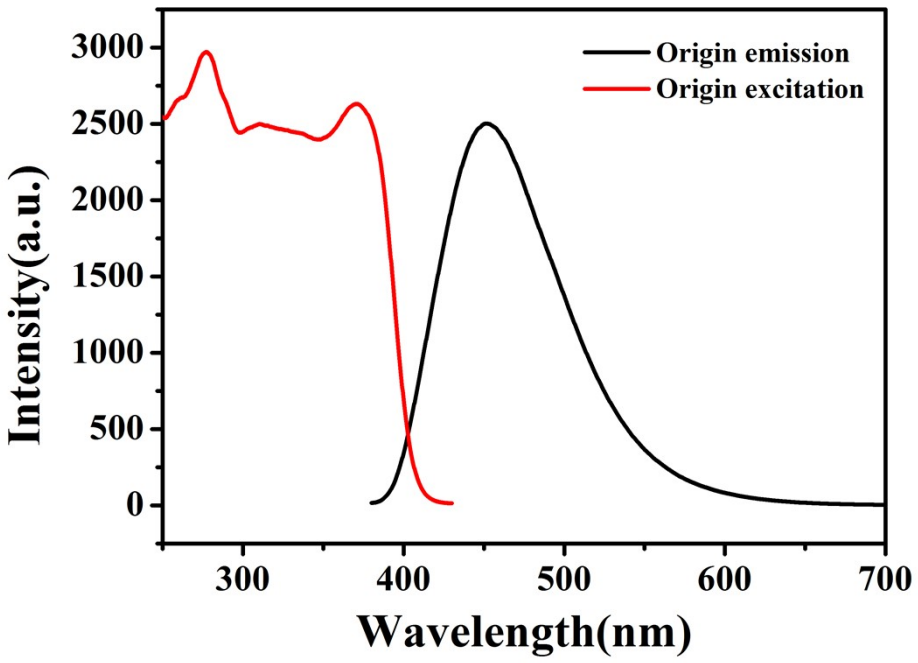


Figure S4. Excitation spectrum (red) and emission spectrum (black) of CJLU-1 ethanol solution.

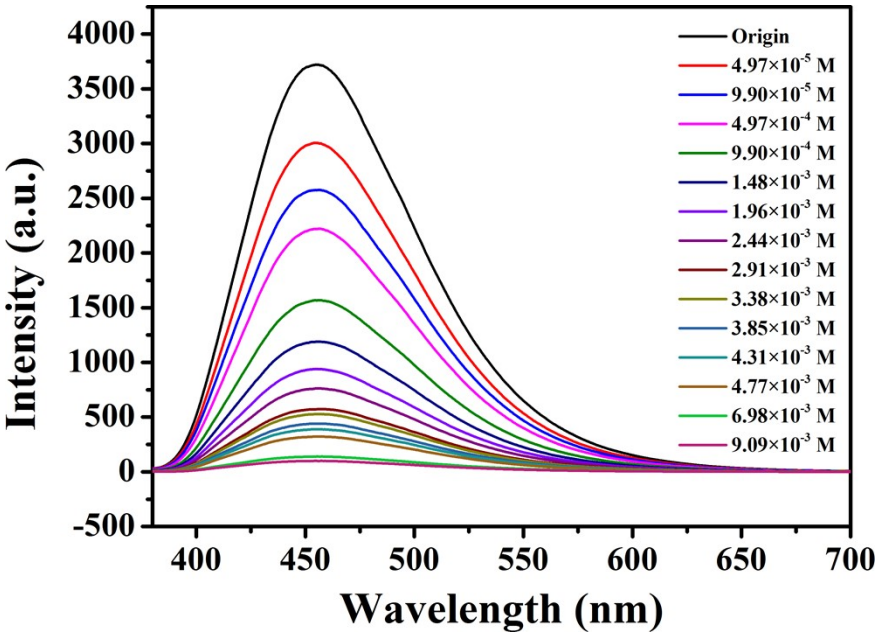


Figure S5. The PL spectrum of CJLU-1 with different amounts of 2,4-DNT.

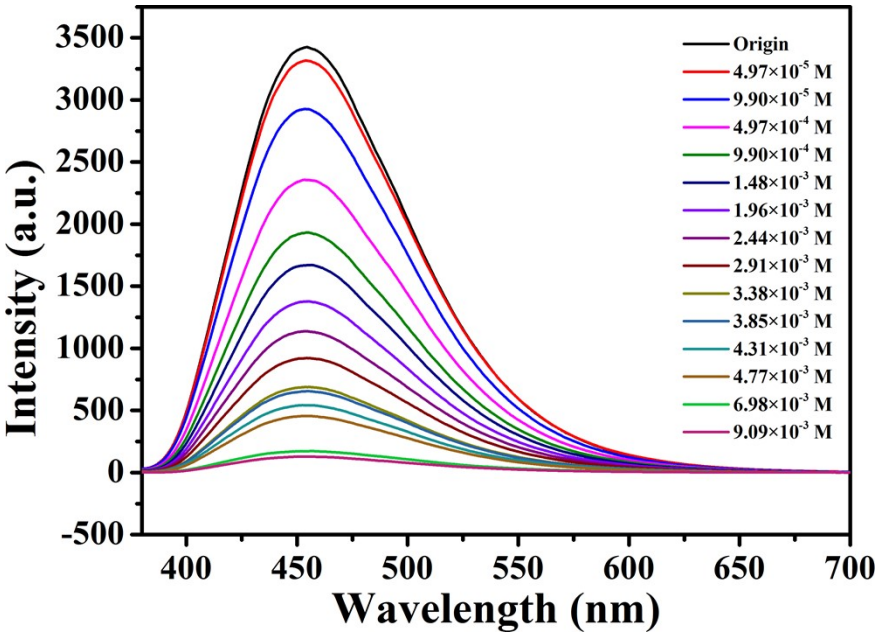


Figure S6. The PL spectrum of CJLU-1 with different amounts of 2,6-DNT.

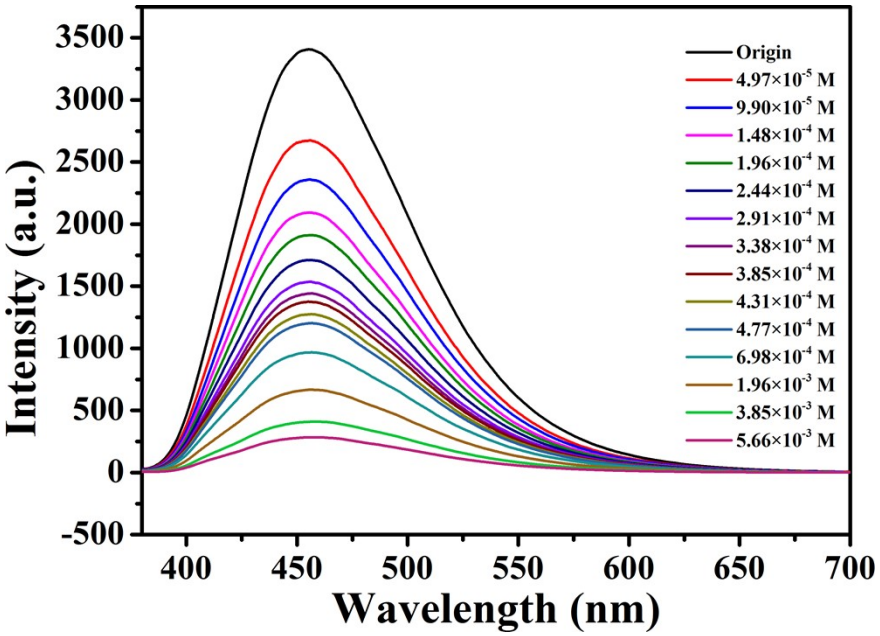


Figure S7. The PL spectrum of CJLU-1 with different amounts of NB.

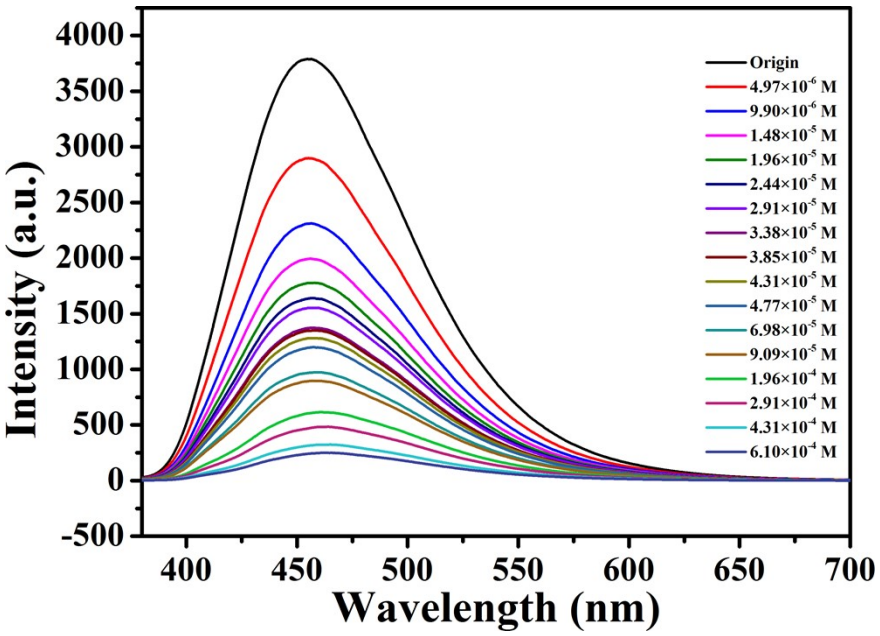


Figure S8. The PL spectrum of CJLU-1 with different amounts of PNP.

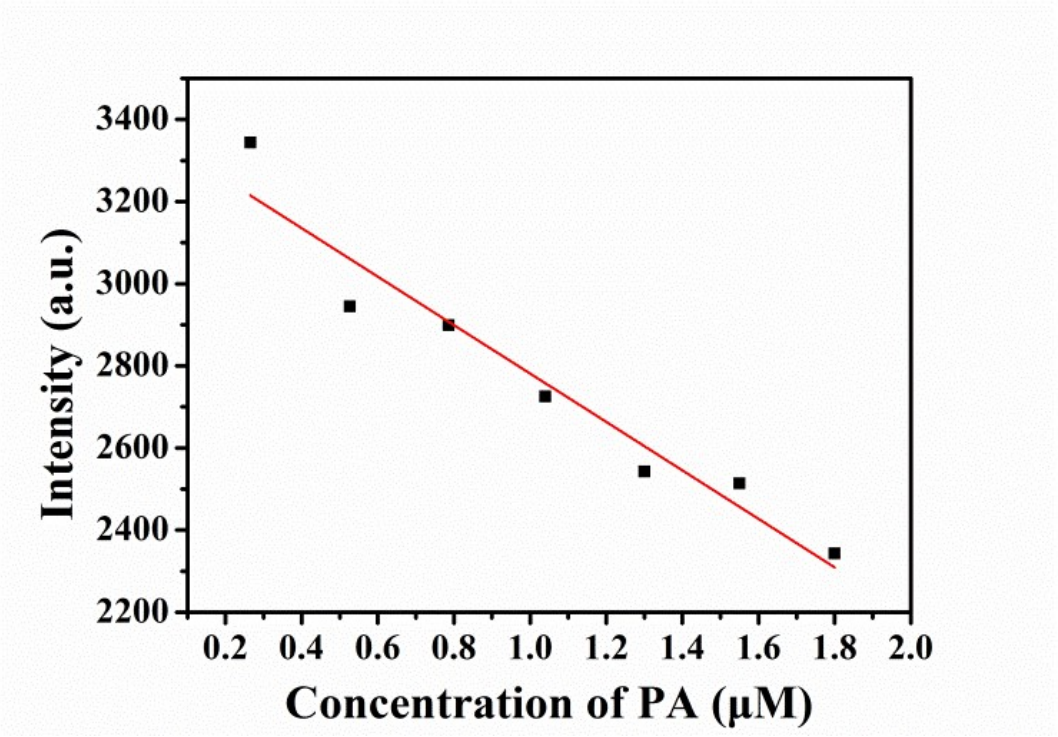


Figure S9. The fit curve of CJLU-1 emission intensity at different PA concentrations.

Linear Equation: Y=-589.893X+3371.478

S=5.89893×10^8 M^{-1}

I_a= $\frac{3083+3305+3282+3232+3328+3261+3320+3302+3287+3239}{10}$ =3263.9

S_b=$\sqrt{\frac{\sum(I_0-I_a)^2}{N-1}}$ =71.20 (N=10)

LOD= $\frac{3\times S_b}{S}$ $\frac{3\times 71.20}{5.89893\times 10^8}$=0.362 μM

S is the slope of the calibration curve, S_b is the standard deviation of the blank group, I_0 is the fluorescence intensity of the MOF solution, and I_a is the average of I_0.

Table S2. The quenching coefficient of reported sensor and Zr-TCA for detecting PA.

Materials	Ksv (M^{-1})	Ref.
[Zn(NH_2-bdc)(4-4'-bpy)]	3.108×10^4	[1]
Tb-CP(1)	38145	[2]
{Cd(INA)(pytpy)(OH)·$2H_2O$}c_n	4.3×10^4	[3]
Complex 3	1.66×10^5	[4]
[Me_2NH_2][Zn_6(qptc)$_3$(trz)$_4$] ·$6H_2O$	4.39×10^4	[5]
[Mg(ATDC)$_4$(H_2O)$_2$]	4.32×10^5	[6]
[Zn(L)(H_2O)] ·H_2O	2.03×10^4	[7]
CP1	2.16×10^4	[8]
CP2	1.52×10^4	[9]
MOF-2	1.36×10^4	[9]
USTC-7	4.9×10^4	[10]
[Zn_2(TPOM)(NH_2-BDC)$_2$]·$4H_2O$	4.6×10^4	[11]
[$(CH_3)_2NH_2$]$_3$[Zn_4Na(BPTC)$_3$] ·$4CH_3OH$·2DMF	3.2×10^4	[12]
JUC-135	3.7×10^4	[13]
[Cd(NDC)$_{0.5}$(PCA)] ·G_x	2.9×10^4	[14]
[Eu_3(bpydb)$_3$(HCOO)(μ_3-OH)$_2$(DMF)] ·(DMF)$_3$(H_2O)$_2$	1.5×10^4	[15]
triphenylamine (TPA) functionalized carboxylic acids(compounds 1-4)	9.715×10^5	[16]
Zr-TCA	2.6×10^5	This work

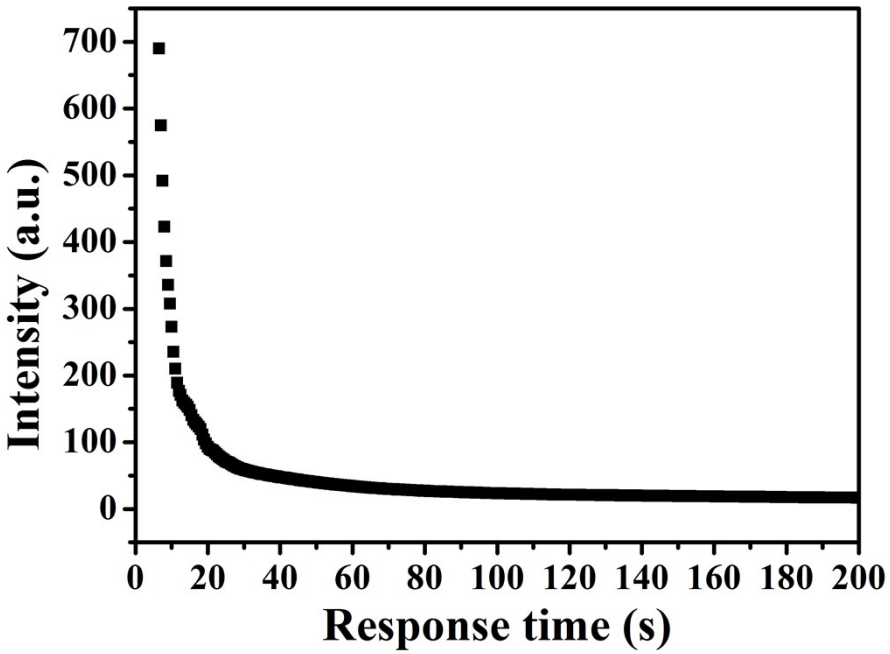


Figure S10. Variation of fluorescence intensity of CJLU-1 at 455 nm with time after the addition of 2.65×10^{-4} M PA.

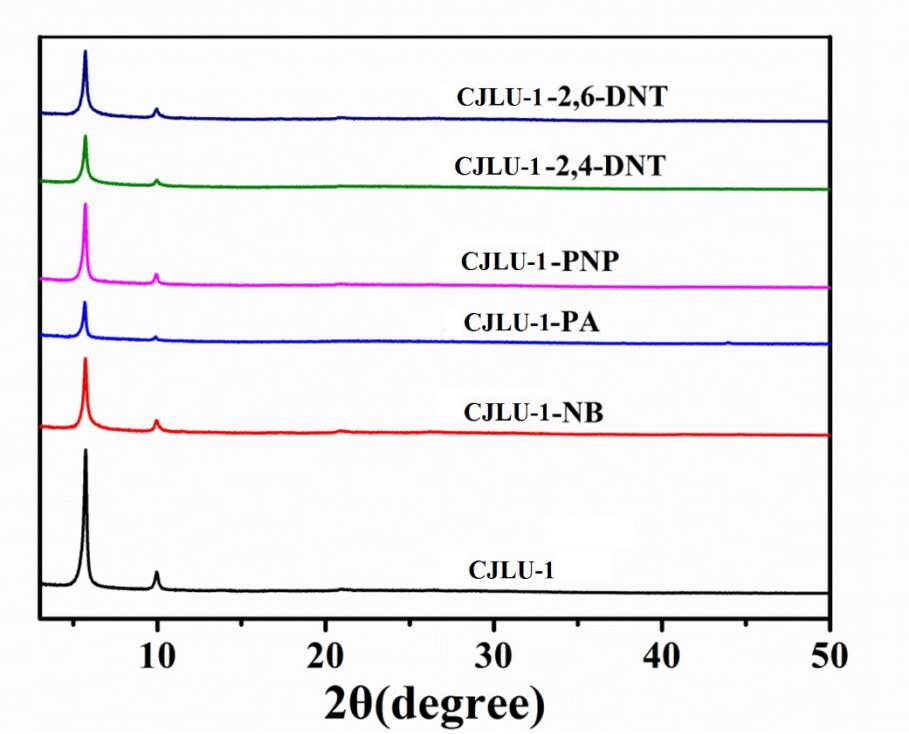
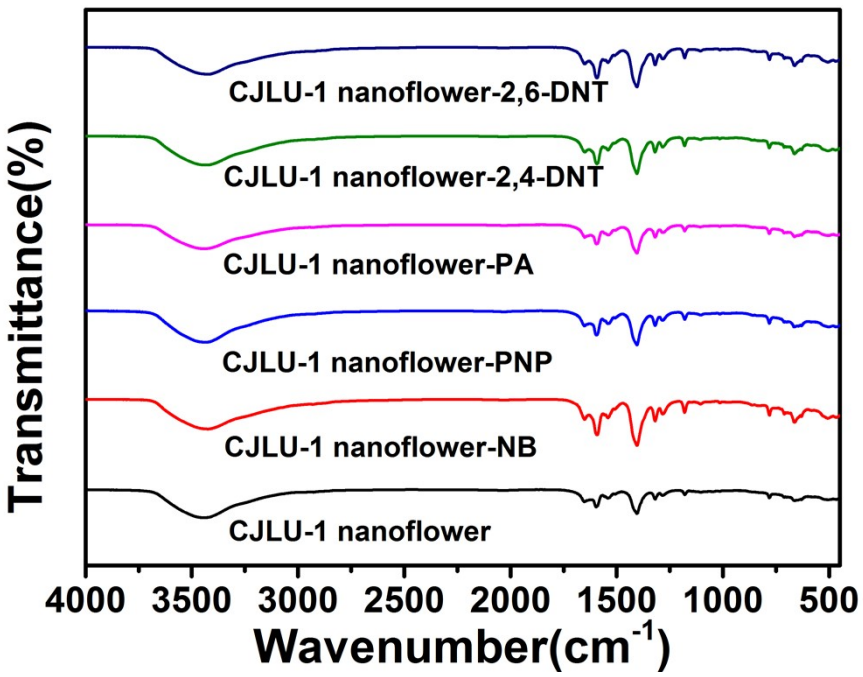


Figure S11. PXRD of CJLU-1 and CJLU-1 with addition of a large amount (10^{-3} M) of nitroaromatics (among them, the concentration of PA was 5.32×10^{-4} M).



Figuer S12. The FT-IR of CJLU-1 and CJLU-1 with addition of a large amount (10^{-3} M) of nitroaromatics (among them, the concentration of PA was 5.32×10^{-3} M).

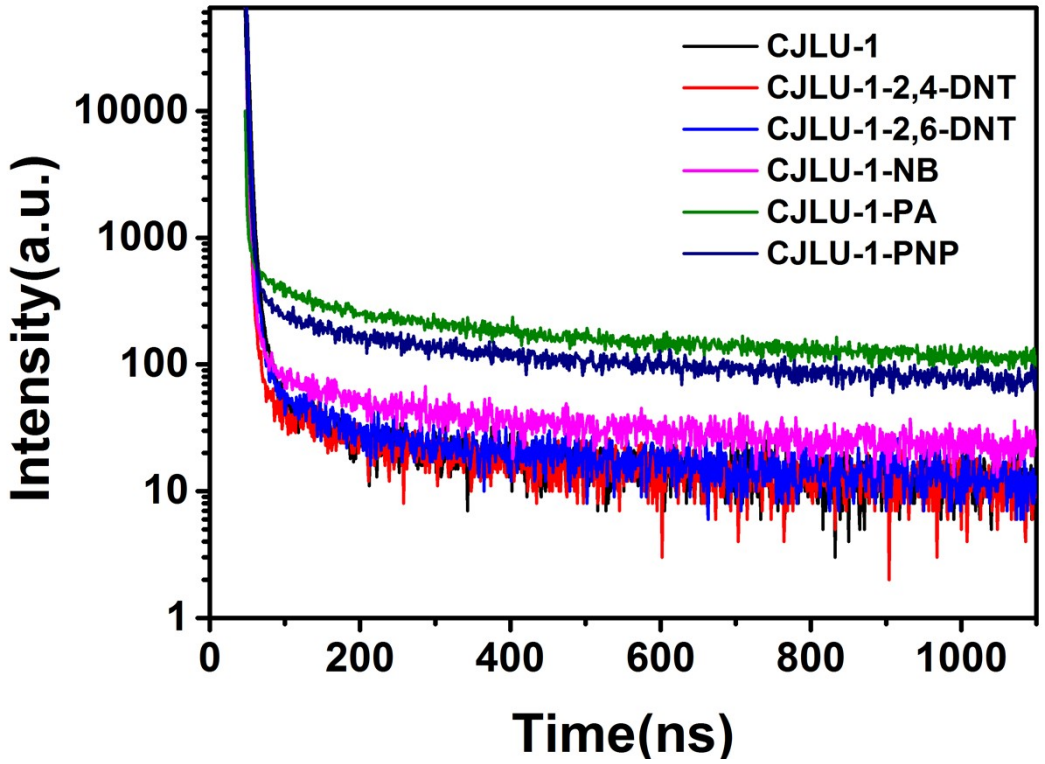


Figure S13. Decay curve of CJLU-1 ethanol solution and CJLU-1 ethanol solution with nitroaromatics concentration of 9.90×10^{-4} M (among them, the concentration of PA was 5.27×10^{-4} M).

Table S2. The fluorescence lifetime of the original CJLU-1 solution and the CJLU-1 solution which was added nitroaromatics.

Small molecule	τ1(ns)
Origin	51.38
2,4-DNT	49.18
2,6-DNT	50.72
NB	49.23
PNP	49.27
PA	48.78

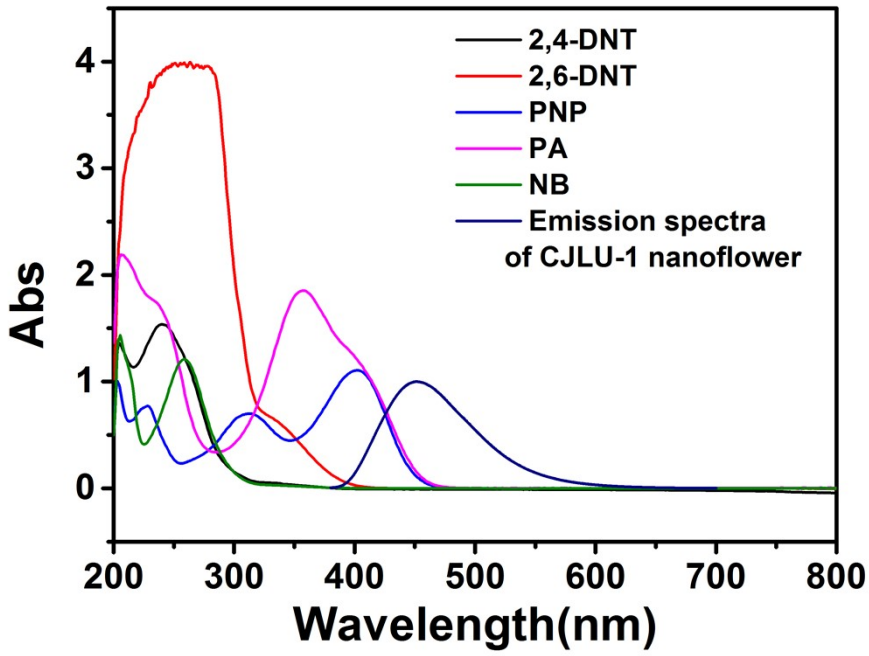


Figure S14. Absorption spectrums of nitroaromatics and emission spectrum of CJLU-1.

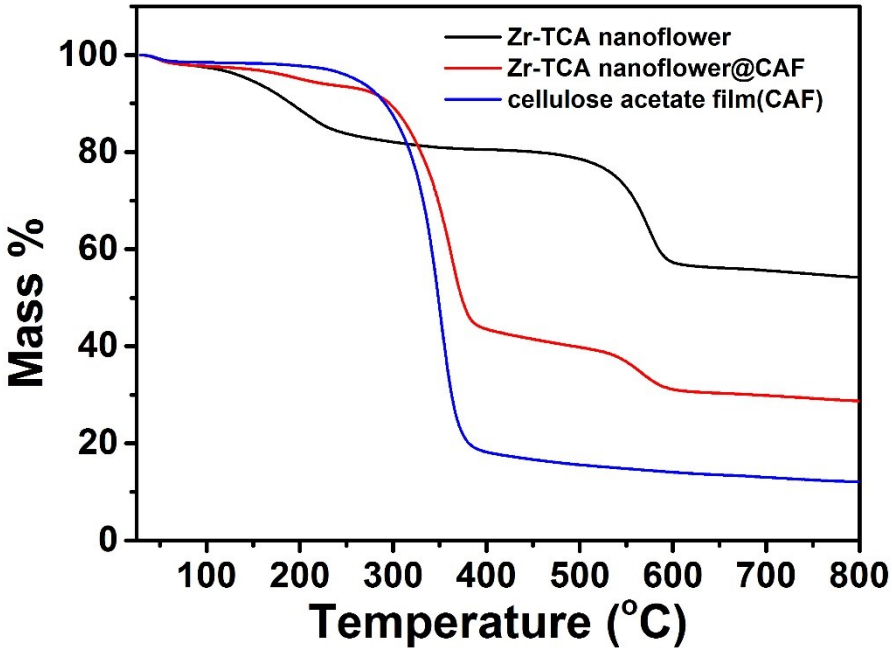


Figure S15. TG curves of CJLU-1, CJLU-1 MMMs and cellulose acetate membrane.

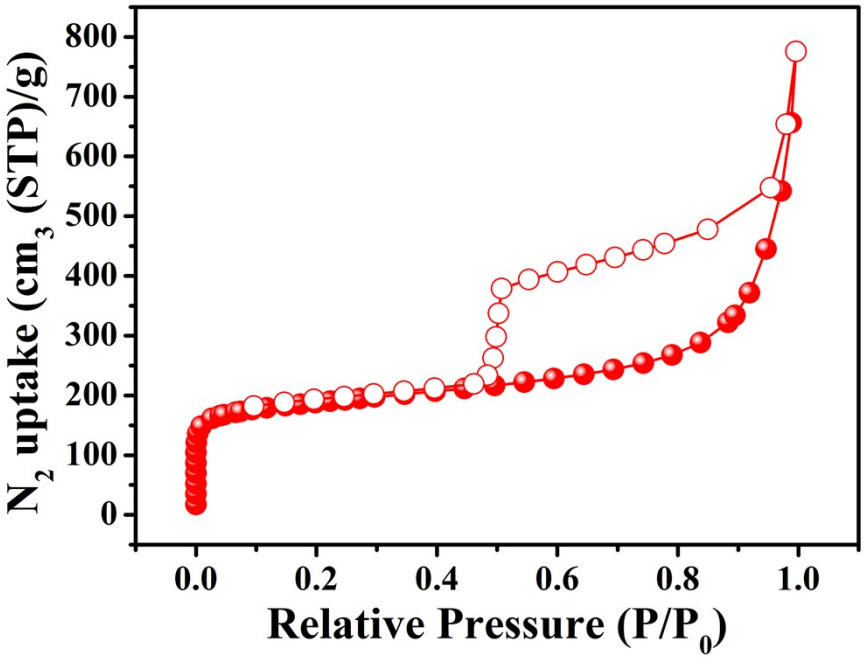


Figure S16. The N_2 adsorption–desorption isotherm of CJLU-1.

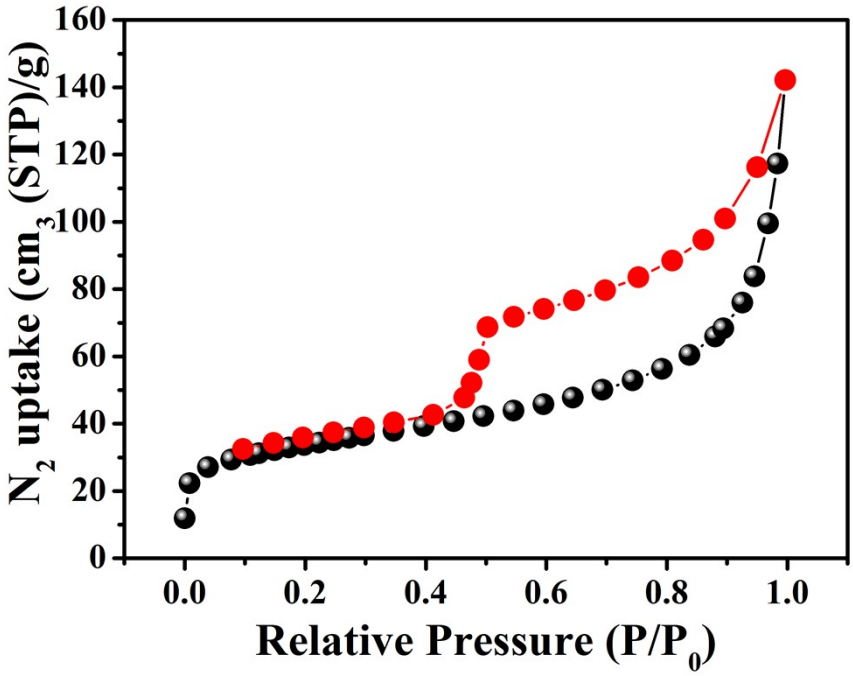


Figure S17. The N_2 adsorption–desorption isotherm of CJLU-1 MMMs.

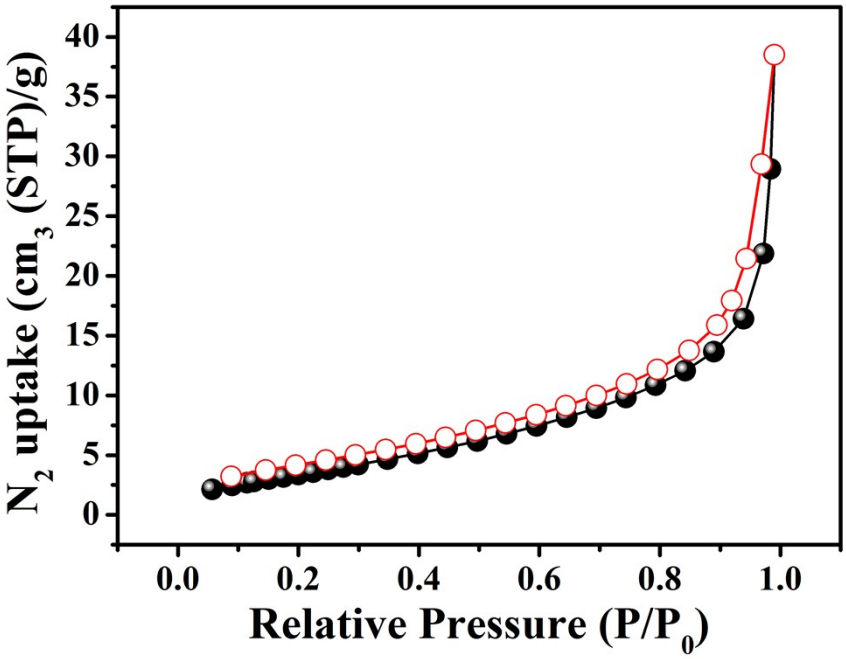


Figure S18. The N_2 adsorption–desorption isotherm of cellulose acetate membrane.

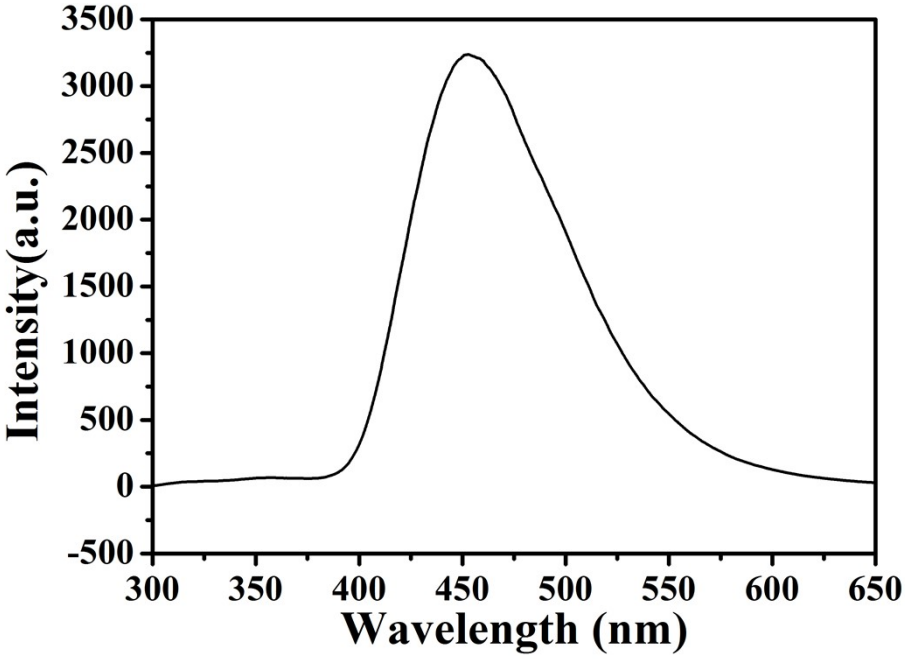


Figure S19. PL spectrum of CJLU-1 MMMs.

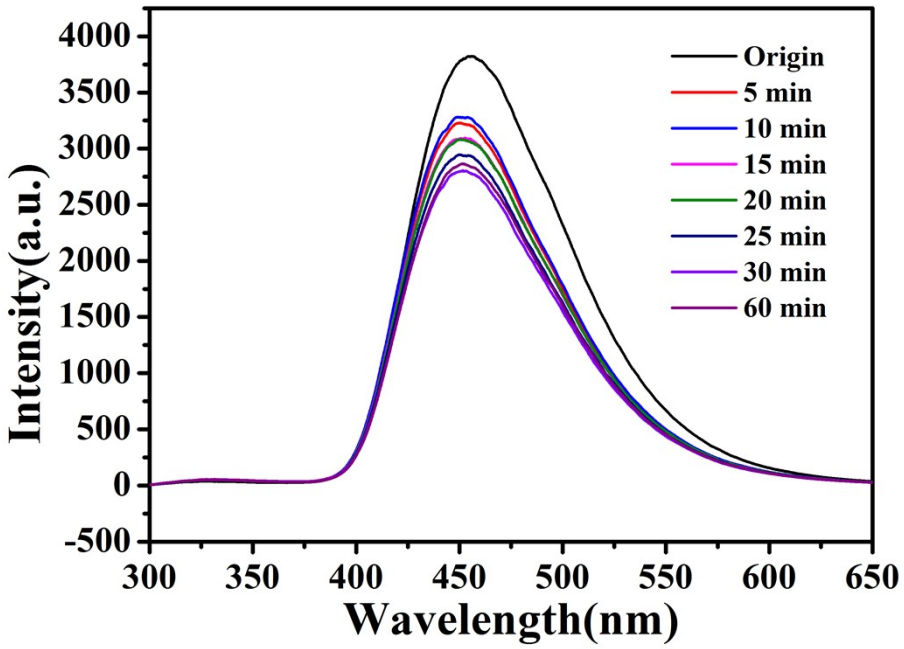


Figure S20. PL of CJLU-1 MMMs detect vapor of PNP.

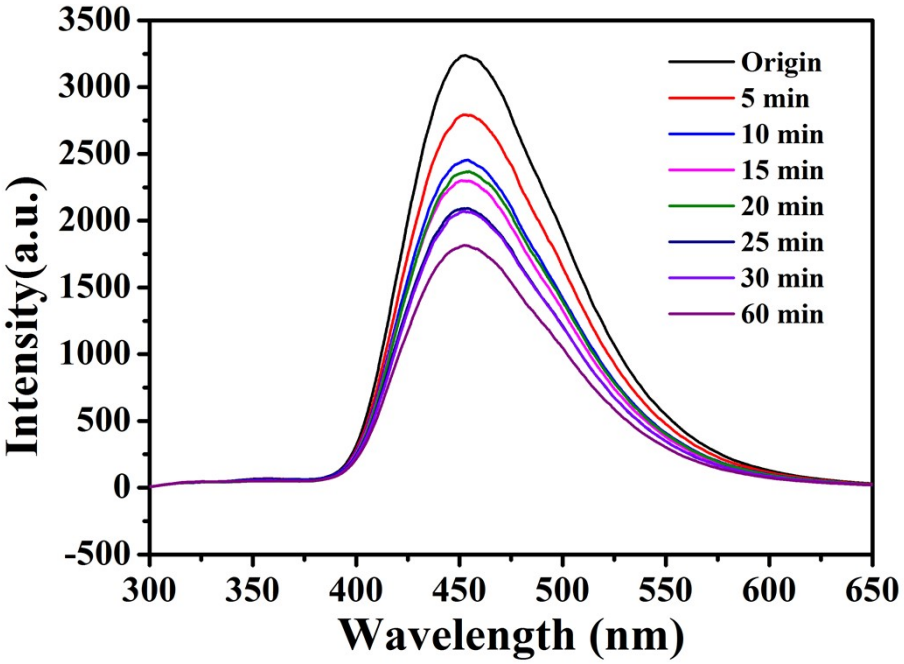


Figure S21. PL of CJLU-1 MMMs detect vapor of 2-nitrotoluene.

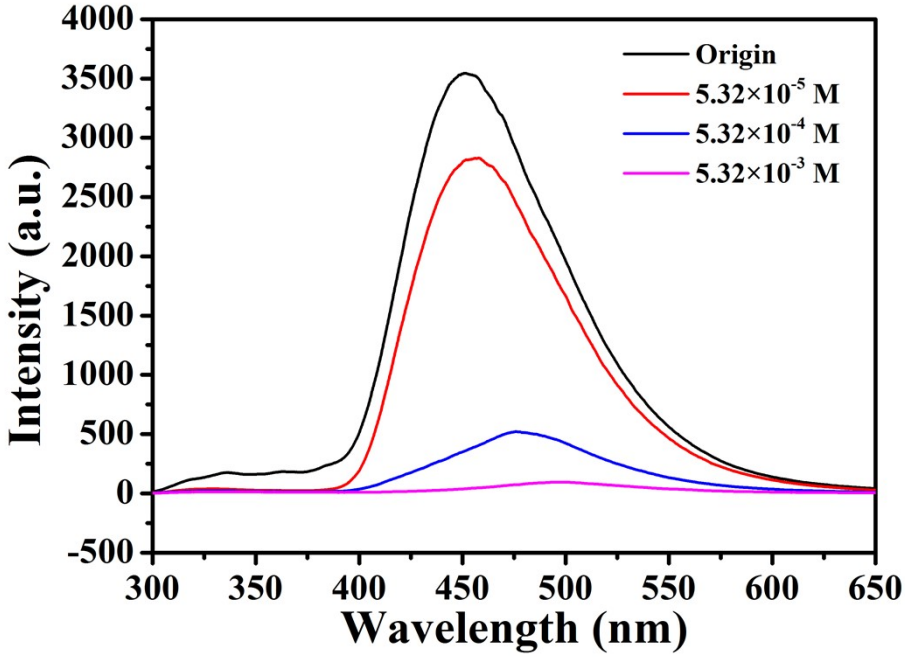


Figure S22. PL of CJLU-1 MMMs detect different concentrations of PA.

References

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