SUPPLEMENTARY INFORMATION

Nanoscale Metal-organic Framework as Highly Sensitive Luminescent Sensor

for Fe²⁺ in aqueous solution and living cell

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Experimental details

Synthetic procedures

Chemicals. Chemicals were purchased from commercial sources. All solvents were analytical grade and without further purification. **Characterization.** The elemental analyses of nitrogen and carbon element the hybrids are measured with a Vario ELIII elemental analyzer. X-ray diffraction patterns (PXRD) are recorded on a Rigaku D/ max-Rb diffractometer equipped with a Cu anode in a 2θ range from 5 to 45°. Transmission electron microscope (TEM) experiments were conducted on a JEOL2011 microscope operated at 200 kV or on a JEM-4000EX microscope operated at 400 kV. Nitrogen adsorption/desorption isotherms are measured by using a Nova 1000 analyzer under the liquid nitrogen temperature. Luminescence excitation and emission spectra of the samples are obtained on Edinburgh FLS920 spectrophotometer. The data of life time is achieved from fitting the experiment luminescent decay. UV-visible diffuse reflectance spectrum was taken with BWS003. X-ray photoelectron spectra (XPS) are recorded under ultra high vacuum (< 10⁻⁶ Pa) at a pass energy of 93.90 eV on a Perkin Elmer PHI 5000C ESCA system by using Mg Ka (1253.6 eV) anode. All binding energies are calibrated by using contaminant carbon (C 1s = 284.6 eV). Size distribution was determined on a Zetasizer Nano ZS90 instrument.

MOF-253 (*a*). 2,2'-Bipyridine-5,5'-dicarboxylic acid (153 mg, 0.625 mmol) was added to a 15 mL centrifuge tube. Then acetic acid (86 mg, 1.875mol) was added. Al(NO₃)₃·9H₂O (151 mg, 0.625 mmol) was added to a separate 10 mL centrifuge tube. The volume in each tube was increased to a total of 7.5 mL by addition of DMF. Both tubes were sonicated for 2 minutes to ensure even dispersion. Then, contents from both tubes were mixed in a 20 mL Teflon-capped pressure vessel, sealed and left to react in an oven at 120 °C. After 3 days, the resulting mixture was collected by centrifugation at 13000 rpm for 10 minutes. The supernatant was decanted leaving white solid. The solid was washed with methanol via soxhlet extraction for 24 h, after which the powder was collected by centrifugation and heated at 200 °C under dynamic vacuum for 12 h. Yield (139 mg, 81 %). IR: 3290 (br w), 1567 (s), 1543 (w), 1475 (m), 1429 (s), 1369 (m), 1247 (w), 1171 (w), 1121 (w), 1054 (w), 1025 (w), 989 (s), 856 (w), 786 (s), 709 (m). Anal. Calcd. for $C_{12}H_7AIN_2O_5$: C, 50.34; H, 2.45; N, 9.79. Found: C, 50.35; H, 2.50; N, 9.75.

MOF-253 (**β**). 2,2'-Bipyridine-5,5'-dicarboxylic acid (153 mg, 0.625 mmol) was added to a 15 mL centrifuge tube. Al(NO₃)₃·9H₂O (151 mg, 0.625 mmol) was added to a separate 10 mL centrifuge tube. The volume in each tube was increased to a total of 7.5 mL by addition of DMF. Then, contents from both tubes were mixed in a 20 mL Teflon-capped pressure vessel, sealed and left to react in an oven at 120 °C. The process is similar to MOF-253 (α). Yield (134 mg, 78 %). IR: 3291 (br w), 1570 (s), 1544 (w), 1475 (m), 1429 (s), 13697 (m), 1248 (w), 1171 (w), 1121 (w), 1051 (w), 1021 (w), 989 (s), 859 (w), 786 (s), 705 (m). Anal. Calcd. for C₁₂H₇AlN₂O₅: C, 50.34; H, 2.45; N, 9.79. Found: C, 50.31; H, 2.51; N, 9.71.

MOF-253 (γ). 2,2'-Bipyridine-5,5'-dicarboxylic acid (153 mg, 0.625 mmol) was added to a 15 mL centrifuge tube. Then sodium acetate (153 mg, 1.875 mmol) was added. Al(NO₃)₃·9H₂O (151 mg, 0.625 mmol) was added to a separate 10 mL centrifuge tube. The volume in each tube was increased to a total of 7.5 mL by addition of DMF. Then, contents from both tubes were mixed in a 20 mL Teflon-capped pressure vessel, sealed and left to react in an oven at 120 °C. After 3 days, the resulting mixture was collected by centrifugation at 13000 rpm for 10 minutes. The mixture is refluxed in methanol one week, and the methanol is refreshed in every 12 hours. The powder was collected by centrifugation and heated at 200 °C under dynamic vacuum for 12 h. Yields (71.1 mg, 40 %). IR: 3290 (br w), 1569 (s), 1543 (w), 1475 (m), 1424 (s), 1366 (m), 1249 (w), 1176 (w), 1125 (w), 1054 (w), 1025 (w), 989 (s), 856 (w), 789 (s), 705 (m). Anal. Calcd. for C₁₂H₇AlN₂O₅: C, 50.34; H, 2.45; N, 9.79. Found: C, 50.31; H, 2.55; N, 9.73.

Cell culture. The Hela cell line was provided by the Institute of Biochemistry and Cell Biology, SIBS, CAS (China). The cells were grown in RPMI 1640 supplemented with 10 % FBS (fetal bovine serum) at 37 °C and 5 % CO₂. Cells (1×10^5 cells mL⁻¹) were plated on 14 mm glass cover slips and allowed to adhere for 24 hrs.

Fluorescence imaging. Experiments to assess Fe^{2+} and Fe^{3+} uptake was performed over 1 h in the same medium supplemented with 50 μ M FeCl₂ or FeCl₃. Before the experiments, Hela cells were washed with PBS buffer, and then the cells were incubated with 5 μ M MOF-253 (γ) in PBS for 3 hrs at 37 °C. Cell imaging was then carried out after washing the cells with PBS. Confocal fluorescence imaging was performed with an OLYMPUS IX81 laser scanning microscope and a 60P oil-immersion objective lens. Cells loaded with MOF-253 (γ) were excited at 405 nm using a HeNe laser.

Absolute quantum yield (QY). Absolute quantum yield (QY) of nMOF-253s measurements is made by exciting the liquid samples

with diffuse light within an integrating sphere under the excitation at 390 nm. The liquid sample is prepared by dispersing nMOF-253s into aqueous (50 mg/L). The outer luminescent quantum efficiency was determined using an integrating sphere (150 mm diameter, $BaSO_4$ coating) from Edinburgh FLS920 phosphorimeter. The spectra were corrected for variations in the output of the excitation source and for variations in the detector response. The quantum yield can be defined as the integrated intensity of the luminescence signal divided by the integrated intensity of the absorption signal. The absorption intensity was calculated by subtracting the integrated intensity of the light source with the sample in the integrating sphere from the integrated intensity of the light source with a blank sample in the integrating sphere.

Photoluminescence measurements. The photoluminescence is record on liquid sample, which is prepared by dispersing nMOF-253s into aqueous (50 mg/L).

Stern–Volmer equation:

$$\frac{I_0}{I} = 1 + Ksv[M]$$

 I_0 and I are the fluorescent intensity before and after the incorporation of metal ion, respectively. [*M*] is molar concentration of metal ion. K_{SV} is the coefficient of quenching. The reduction of fluorescent intensity is proportional to metal ion concentration. K_{SV} can be calculated via fluorescent data.



Figure S1. PXRD for MOF-253-based material; the inset is the representative structure of MOF-253 with subsequent insertion of metal ion into open bipyridine ligand sites. Orange octahedra represent Al atoms, while red, blue, and gray spheres represent O, N, and C atoms, respectively, H atoms are omitted for clarity. The inset is drawn by using structural data taken from the literature.^{S1}



Figure S2. The selected area electron diffraction pattern (SAED), a for MOF-253 (α), b for Mof-253 (β) and c for MOF-253 (γ). The stability of MOF is usually weaker than the traditional inorganic nanocrystal. It is hardly to archieve singal crystal electron diffraction. So we selecte a broad area to archieve polycrystal electron diffraction.



Figure S3. DLS curve of MOF-253 (α), Mof-253 (β) and MOF-253 (γ).



Figure S4. N₂ adsorption-desorption isotherms of MOF-253 nanocrystal, MOF-253 (MOF-253 (α), MOF-253 (β) and MOF-253 (γ) were calculated to be 1092, 1183 and 1272 m²/g, the Langmuir surface areas of MOF-253 is consistent with reported literature.^{S2}



Figure S5. (a) The excitation and emission spectra of nMOF-253s, $\lambda_{em} = 545$ nm and $\lambda_{ex} = 390$ nm and the CIE plot of MOF-253 (γ) (b).



Figure S6. Decay curve of MOF-253 (α) for a, MOF-253 (β) for b and MOF-253 (γ) for c (the λ_{em} = 545 nm and the λ_{ex} = 390 nm).



Figure S7. Comparison of the fluorescence intensity of different metal ion incorporated MOF-253 (γ) (50 mg/L) activated in 100 μ M M^{X+} (X = 1, 2 or 3) aqueous solution (M^{x+=} Na⁺, Ba²⁺, Ca²⁺, Mg²⁺, Pd²⁺, Zn²⁺, Cd²⁺, Ni²⁺, Co²⁺, Cu²⁺, Cr³⁺, Fe²⁺, Fe³⁺), $\lambda_{ex} = 390$ nm



Figure S8. The luminescence change after the addition of Fe²⁺ ion (100 μ M) on MOF-253 (γ) under UV light (λ_{ex} = 365 nm).



Figure S9. Comparison of the fluorescence intensity of different metal ion incorporated MOF-253 (α) (a) and MOF-253 (β) (b) (50 mg/L) activated in 100 μ M M^{X+} (X = 1, 2 or 3) aqueous solution. *I* and *I*₀ denote the fluorescence intensity of MOF-253 (α) or MOF-253 (β) with and without metal ions, respectively; the emission spectra of MOF-253 (α) (c) and MOF-253 (β) (d) in the aqueous with metal ion (Na⁺, Ba²⁺, Ca²⁺, Mg²⁺, Pd²⁺, Zn²⁺, Cd²⁺, Ni²⁺, Co²⁺, Cu²⁺, Cr³⁺, Fe³⁺), $\lambda_{ex} = 390$ nm.



Figure S10. The excitation (blue) and emission spectra (brown) of MOF-253 (γ) (excited and monitored at 390 nm and 545 nm, respectively), excitation (black) and emission spectra (red) of H₂bypbc (excited and monitored at 361 nm and 555 nm, respectively)



Figure S11. The PXRD of MOF-253 (γ) after immersed in Fe²⁺ aqueous solution.



Figure S12. XPS spectra for MOF-253(γ) after immersed in Fe²⁺ aqueous solution, the inset is the N 1S region. The binding energy of the N 1S peak of MOF-253 incorporated Fe²⁺ ion (403 eV) is shifted remarkably toward higher binding energy, compared to that of the reported pristine MOF-253 (397 eV).^{S3} Such a big shift reflected a decrease in the electron density of the N atom, which may be attributed to the strong coordination between the bipyridine and Fe²⁺ ion.



Wavelength (nm)

Figure S13. UV-visible diffuse reflectance spectrum (DRS) of different metal ion incorporated MOF-253 (γ) (metal ion: Na⁺, Ba²⁺, Ca²⁺, Mg²⁺, Pd²⁺, Zn²⁺, Cd²⁺, Ni²⁺, Co²⁺, Cu²⁺, Cr³⁺, Fe²⁺, Fe³⁺), the inset is the photograph MOF-253 (γ) with different ion.



Figure S14. The emission spectra of H₂bypdc in the aqueous with Fe²⁺ ($\lambda_{ex} = 361$ nm).



Figure S15. The emission spectra of MOF-253 (γ) with Fe²⁺ ion aqueous solution (100 μ M) and Hemin (100 μ M) aqueous solution (pH = 8.0), $\lambda_{ex} = 390$ nm



Figure S16. (a) The day-to-day fluorescence stability of MOF-253 (γ), $\lambda_{ex} = 390$ nm, and (b) the effect of pH on the fluorescence intensity of MOF-253 (50 mg/L).



Figure S17. In vitro cell viability of HeLa cells incubated with MOF-253 (γ) at different concentrations for 24 hrs.



Figure S18. Z-scan images of HeLa Cells incubated with MOF-253 (γ) (λ_{ex} = 405 nm).



Figure S19. Confocal fluorescence and brightfield images of HeLa cells. (a) Fluorescence image, (b) brightfield image, and (c) overlay image of HeLa cells incubated with 5 μ M MOF-253 (γ) and then supplemented with 50 μ M FeCl₃ in the growth media for 1 hrs at 37 °C (λ_{ex} = 405 nm).

Table S1. Coefficient of quenching (K_{SV}) w	with different metal ion ($(Na^+, Ba^{2+}, Ca^{2+}, M)$	1g ²⁺ , Pd ²⁺ , Zn ²⁺ ,	Cd ²⁺ , Ni ²⁺ ,
$Co^{2+}, Cu^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+})$				

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Metal ion	K_{SV} (M ⁻¹) of MOF-253 (α)	K_{SV} (M ⁻¹) of MOF-253 (β)	K_{SV} (M ⁻¹) of MOF-253 (γ)
Ba^{2+}	221	215	211
Mg^{2+}	359	354	355
Na ⁺	379	377	376
Zn^{2+}	431	426	421
Cd^{2+}	465	458	453
Pb^{2+}	571	566	561
Ni ²⁺	771	768	763
Cr ³⁺	881	879	871
Co^{2+}	878	875	873
Cu^{2+}	999	994	984
Fe ³⁺	1743	1733	1723
Fe ²⁺	26123	24839	23333

Table S2. Comparison of the analytical performance of the fluorescence sensing systems for Fe²⁺

-	Fluorescent	Liner (µM)	Range detection	Refs	
	material	limits (µM)			
	pyrene-TEMPO	0.24-3.6	0.04	S4	
	DansSQ	Not mentioned	3.6	S5	
	BPD-Cy-Tpy	0.1-7.0	Not mentioned	S6	
	MOF-253	5-100	0.5	This work	

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