

Supporting Information

Synthesis of an Ammelide-Based Ultra-microporous Cd-MOF for Sensitive Detection of Dichromate Ions

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Section 1 Materials and Synthetic Procedures

All solvents and materials except ammelide were purchased commercially and used without further purification. 5-Azacytosine was purchased from Adamas-Beta. DMF and Methanol were purchased from Tianjin Damao Chemical Reagent Factory.

Synthesis of Ammelide

2.00g 5-Azacytosine was put into 40mL of acetic acid, and 20.00mL of 30% hydrogen peroxide was added, and heated to 50°C with stirring, and the reaction was carried out for 6h, and then the reaction was allowed to stand at 5°C for 24 hours, and a white precipitate was obtained. Then the white precipitate was filtered out, washed with water and dried to obtain 1.64 g ammelide, with a yield of 71.62%. ¹H NMR (DMSO-d₆, 600 MHz, δ) as shown in Figure S1 10.73, 10.43, and 7.00 ppm, with an integrated area ratio of approximately 1:1:2. Characteristic IR stretching vibrations at 3304, 2861, 2810, 1736, 1700, 1460, 1419, 1267, 1180, 1092, 1042, 987, 908, 869, 660, 566, and 540 cm⁻¹ (Figure S2), which are consistent with previously reported spectrum of ammelide. Infrared absorption spectra show that the stretching vibration at 3500~3300 cm⁻¹ is attributed to R₂N-H and at 1640 cm⁻¹ to R₂C=O. The standard ammelide has stretching vibration peaks at 1180 and 1092 cm⁻¹. This is due to the C-O stretching vibration in the ammelide resonant, while 5-Azacytosine does not have any stretching vibration peaks. This indicates that 5-Azacytosine has been transformed to form ammelide. The UV-Vis absorption peak was observed at 200 nm (Figure S3) for 5-Azacytosine, while the obtained product reveals major absorption peak at 198 nm and 220 nm (Figure S4).

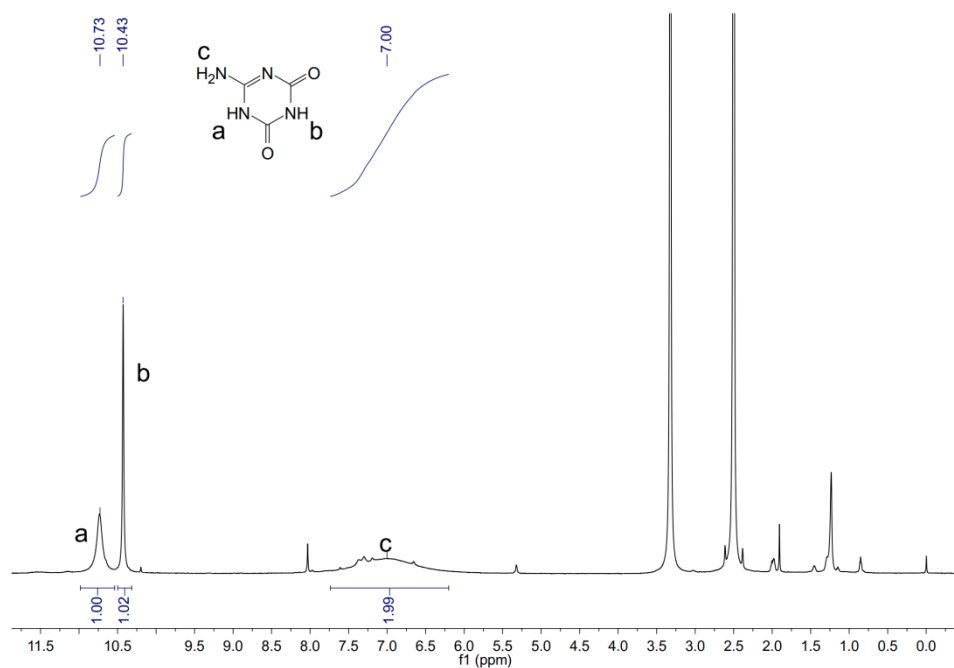


Figure S1. ^1H NMR (600 MHz, DMSO-d_6) spectra of as synthesized ammelide.

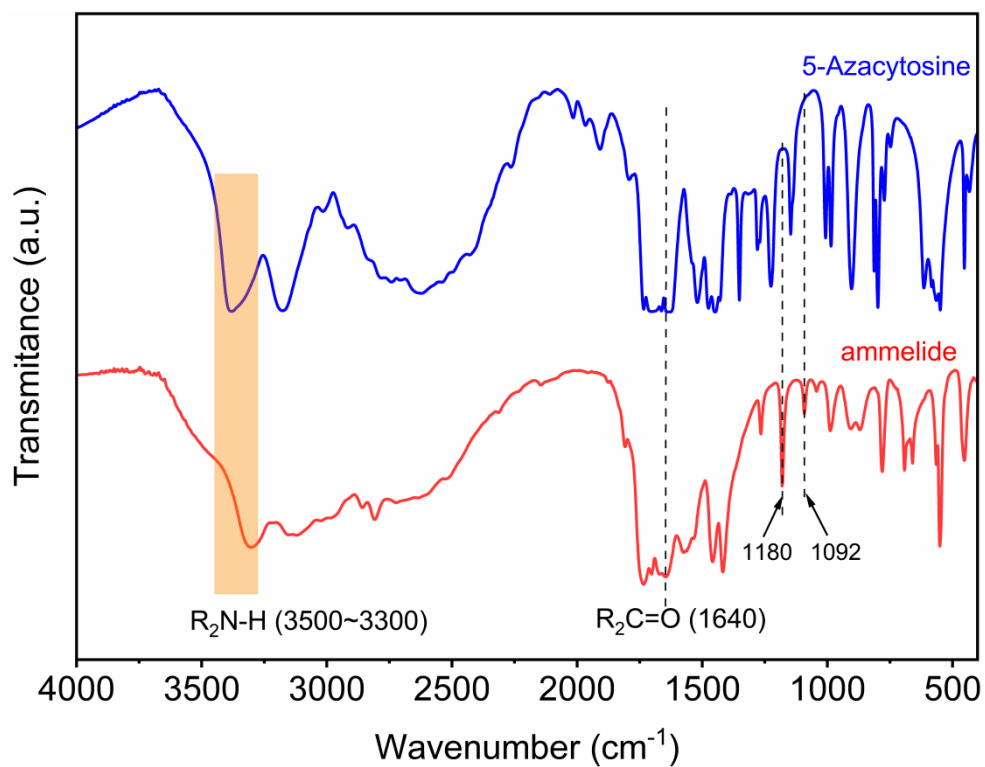


Figure S2. Infrared absorption spectra of 5-Azacytosine and ammelide.

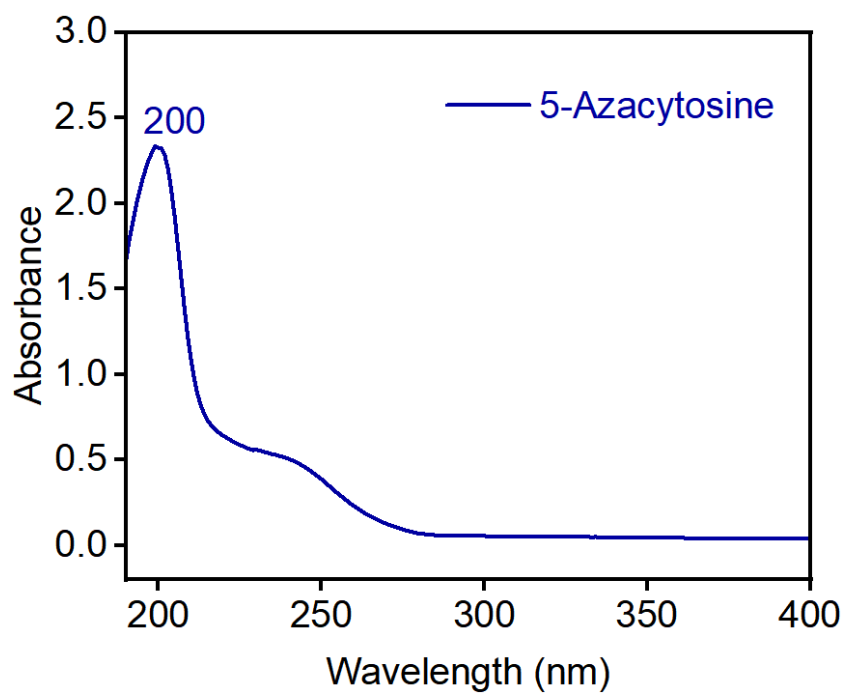


Figure S3. UV-Vis absorption spectrum of 5-Azacytosine .

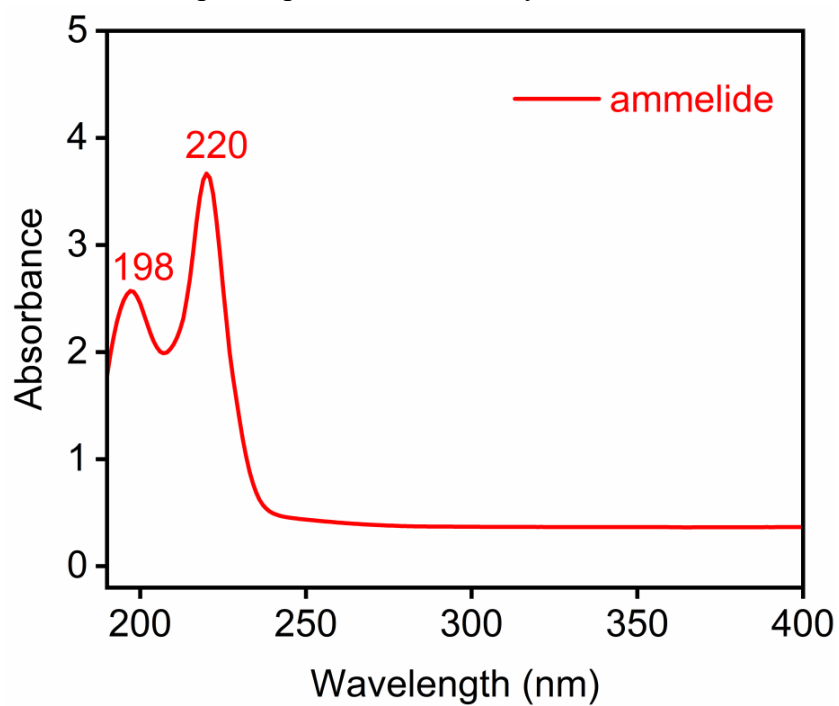


Figure S4. UV-Vis absorption spectrum of ammelide.

Synthesis of SXU-122

A mixture of ammelide (0.1 mmol, 13 mg) and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (1 mol/L, 100 μL) were dissolved in N,N-dimethylformamide/anhydrous methanol (v/v=1:1) (3 mL) and sealed in a glass tube, which was heated at 120°C for 72 hours.

Activated procedure of SXU-122

After filtration, the crystalline SXU-122 was immersed in DMF solution for 3 days, exchanging fresh ethanol solution every day to remove the residual solvent, and then fresh acetone solvent to remove the DMF solvent in the same way. Finally, SXU-122 was vacuum dried at 100°C for 24 h to obtain colorless rod-like SXU-122 with 63% yield.

Section 2 Methods

Characterization

1. PXRD. The PXRD patterns of SXU-122 in different solvents (deionized water, ethanol, DMSO, etc.) were obtained by the following method: 10 mg SXU-122 was immersed in different solvents for specified period of time and filter, milled for PXRD testing. Variable temperature PXRD tests were conducted after heating SXU-122 sample to a specified temperature in a muffle furnace at a rate of 10 °C min⁻¹ first and then stabilizing for 30 min. The Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer with a step width of 1° min⁻¹ in 2 θ using Cu K α ($\lambda = 0.15406$ nm) radiation at 40 kV and 40 mA.

2. Fluorescence experiments. Fluorescence emission and excitation spectra were obtained on a FLS-980 fluorescence spectrometer. We measured solid-state fluorescence emission spectroscopy of activated SXU-122 and ammelide with identical mass under the same conditions. The details of the fluorescence emission

spectra test in the liquid state were as follows, 2 mg of activated SXU-122 was milled, and added to 3 mL of deionized water and sonicated for 45 min. and then transferred to a fluorescence cuvette to test the emission spectra and use it as a blank sample. For anion detection and anti-interference experiments, we added other anions to the blank sample to observe the changes in the fluorescence emission spectra.

3. Gas adsorption measurements. The N₂ gas adsorption isotherms at 77K were obtained on a Quantachrome autosord iQ2 analyzer. We soaked 60 mg of SXU-122 in 10 mL of DMF for three days, exchanging it twice a day with fresh DMF, after which it was immersed in acetone for three days in the same way. Finally, SXU-122 was dried under vacuum at 373 K for 12h. Before measurement, SXU-122 samples were degassed under vacuum at 373 K for 8 h.

4. Infrared absorption spectroscopy of ammelide. We milled 2 mg of ammelide and 200 mg of KBr under the heat of an infrared baking lamp, and a portion of the sample was added to a mold to be pressed, after which it was placed in an infrared absorption spectrometer to obtain the infrared absorption spectrum of ammelide. Infrared absorption spectra were collected on a Fourier Transform Infrared Spectrometer model Nicolette iS5. Before the test, the samples and KBr were dried in an oven at 353 K for 1 h to remove surface water.

5. Thermogravimetry analyses (TG) were performed in the temperature range of 30 – 900 ° C, with a heating rate of 10 ° C min⁻¹ under flowing nitrogen atmosphere on a Netzsch STA 449C simultaneous thermal analyzer.

X-ray crystallographic structure determination of SXU-122

The single crystal data were collected with a Rigaku XtaLab P200 diffractometer and a Dectris Pilatus 200K system at 298 K. The system was equipped with a MicroMax007 HF/VariMax rotating anode X-ray generator with confocal monochromatic Mo-K α radiation. The collected data were solved and refined by full matrix least squares using SHELXL 2016/4.[1] The phases of the synthesized crystals were identified using powder X-ray diffraction (PXRD) method. Based on the single crystal diffraction data, simulated PXRD patterns were generated using Mercury 3.9 software.

Section 3 Supporting Tables

Table S1 Crystallographic parameters of **SXU-122**.

Compound	SXU-122
CCDC	2382000
Empirical formula	C ₆ H ₆ CdN ₈ O ₄ [C ₃ H ₇ NO]
Formula weight	439.69
Temperature (K)	298(2)
Crystal system	trigonal
Space group	<i>P</i> 3 ₁ 21
a (Å)	12.7618(2)
b (Å)	12.7618(2)
c (Å)	7.6340(2)
α (°)	90
β (°)	90
γ (°)	120
Volume(Å ³)	1076.73(4)
Z	3
D _c (g cm ⁻³)	1.696
μ (mm ⁻¹)	1.543
F (000)	534.0
Radiation	Mo-Kα (λ = 0.71073 Å)
Goodness-of-fit on F ²	1.140
Final R indexes ^[a]	R ₁ = 0.0296, wR ₂ = 0.0663
Final R indexes [all data] ^[a]	R ₁ = 0.0311, wR ₂ = 0.0668
Largest diff. peak/hole / e Å ⁻³	1.51/-0.91
$R_1 = \frac{\sum F_0 - F_c }{\sum F_0 }; wR_2 = \left[\frac{\sum w(F_0 ^2 - F_c ^2)^2}{\sum w(F_0^2)^2} \right]^{1/2}$	

Table S2. Comparison with other reported MOF-based fluorescent sensors.

Material	Analytes	Method	Quenching constant, K_{sv}	Ref
Eu-MOF	$Cr_2O_7^{2-}$	Fluorescence	$1.14 \times 10^4 M^{-1}$	[2]
Tb-MOF	$Cr_2O_7^{2-}$	Fluorescence	$8.23 \times 10^3 M^{-1}$	[2]
Zr-MOFs	$Cr_2O_7^{2-}$	Fluorescence	$8.85 \times 10^3 M^{-1}$	[3]
Zn-MOFs	$Cr_2O_7^{2-}$	Fluorescence	$1.18 \times 10^3 M^{-1}$	[4]
Cd-MOFs	$Cr_2O_7^{2-}$	Fluorescence	$6.73 \times 10^5 M^{-1}$	[5]
BUT-39	$Cr_2O_7^{2-}$	Fluorescence	$1.57 \times 10^4 M^{-1}$	[6]
Zr-MOFs	$Cr_2O_7^{2-}$	Fluorescence	$6.49 \times 10^4 M^{-1}$	[7]
Zr-MOFs	$Cr_2O_7^{2-}$	Fluorescence	$6.88 \times 10^3 M^{-1}$	[8]
Zn-MOFs	$Cr_2O_7^{2-}$	Fluorescence	$7.59 \times 10^3 M^{-1}$	[9]
Tb-MOFs	$Cr_2O_7^{2-}$	Fluorescence	$1.01 \times 10^4 M^{-1}$	[10]
Eu-MOFs	$Cr_2O_7^{2-}$	Fluorescence	$0.72 \times 10^4 M^{-1}$	[10]
Eu-MOFs	$Cr_2O_7^{2-}$	Fluorescence	$8.98 \times 10^3 M^{-1}$	[11]
IUST-1	$Cr_2O_7^{2-}$	Fluorescence	$3.31 \times 10^4 M^{-1}$	[12]
Pb-MOFs	$Cr_2O_7^{2-}$	Fluorescence	$2.56 \times 10^3 M^{-1}$	[13]
SXU-122	$Cr_2O_7^{2-}$	Fluorescence	$2.93 \times 10^4 M^{-1}$	this work

Section 4 Supporting Figures

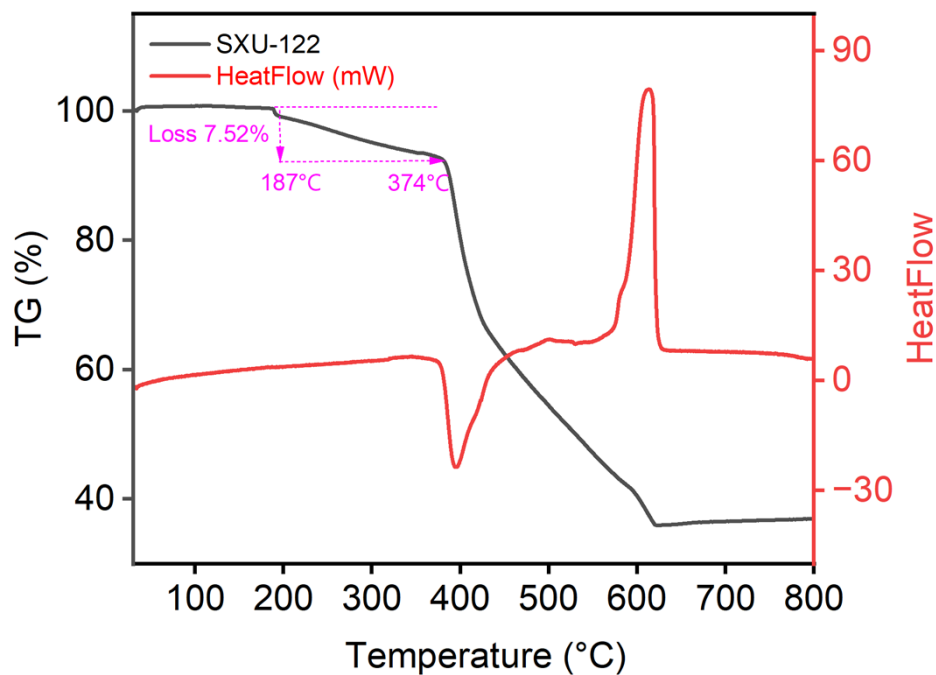


Figure S5. The TG and heat flow curves of the unactivated SXU-122

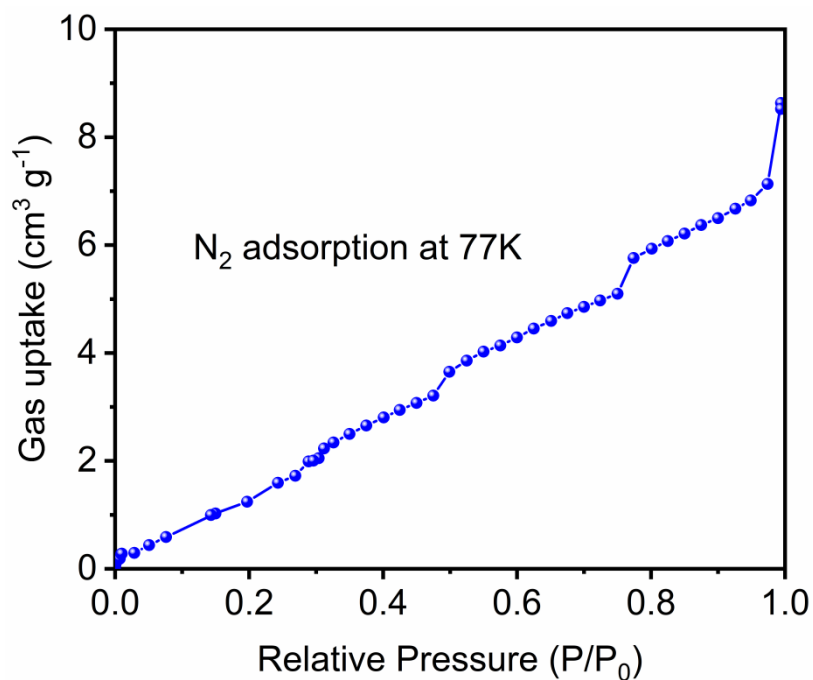


Figure S6. N₂ adsorption isotherm at 77K of SXU-122.

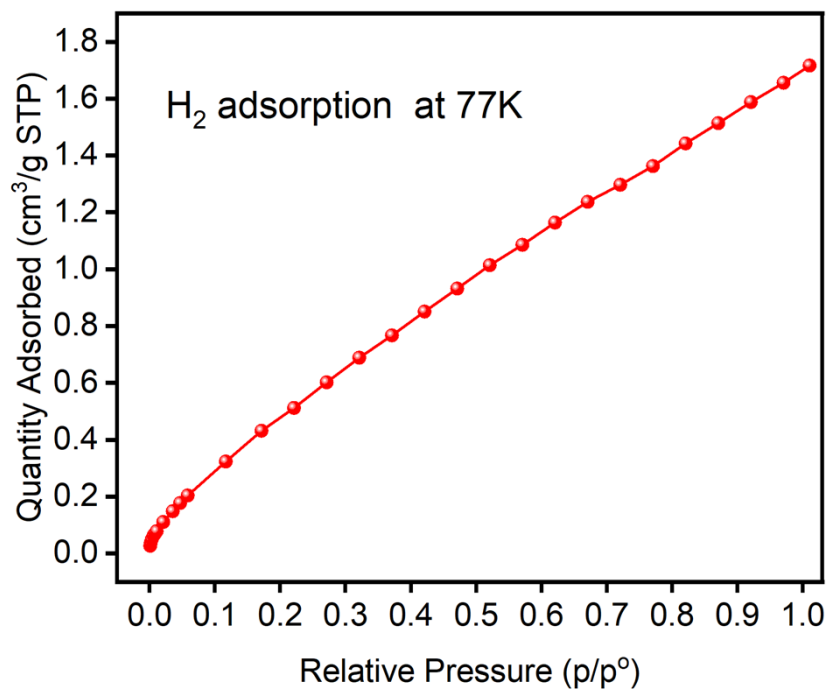


Figure S7. H₂ adsorption isotherm at 77K of SXU-122.

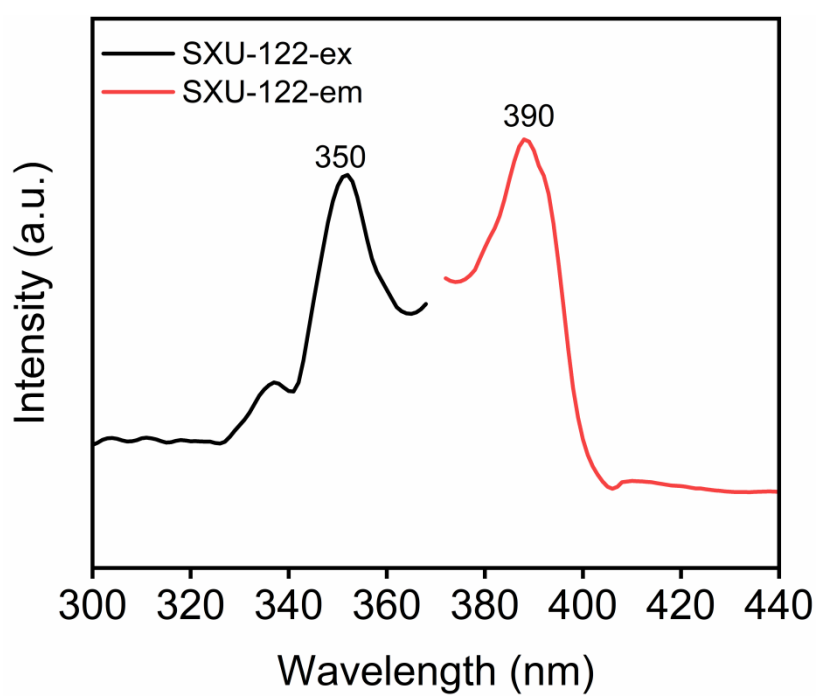


Figure S8. Excitation and emission spectra of SXU-122.

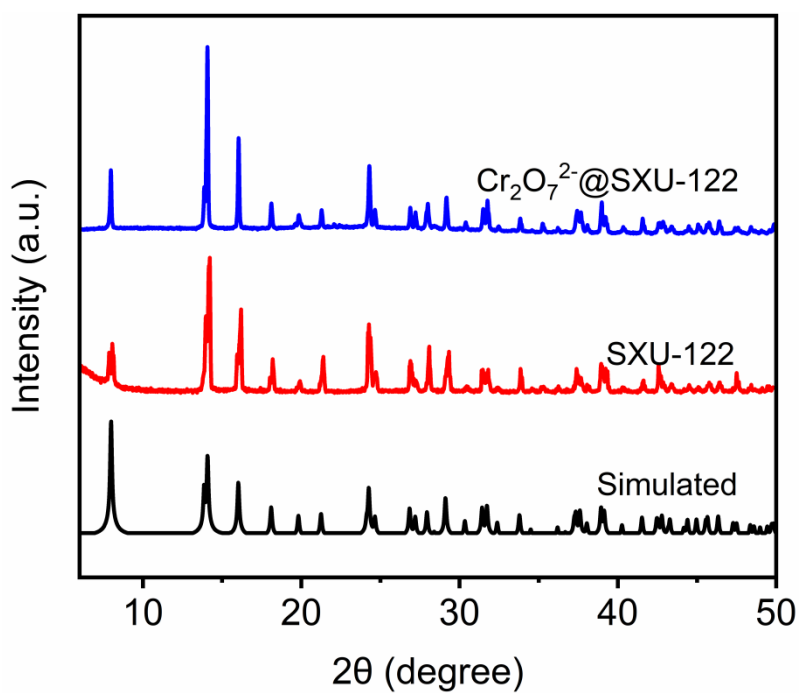


Figure S9. PXRD patterns simulated SXU-122, as-synthesized SXU-122 and $\text{Cr}_2\text{O}_7^{2-}@SXU-122$.

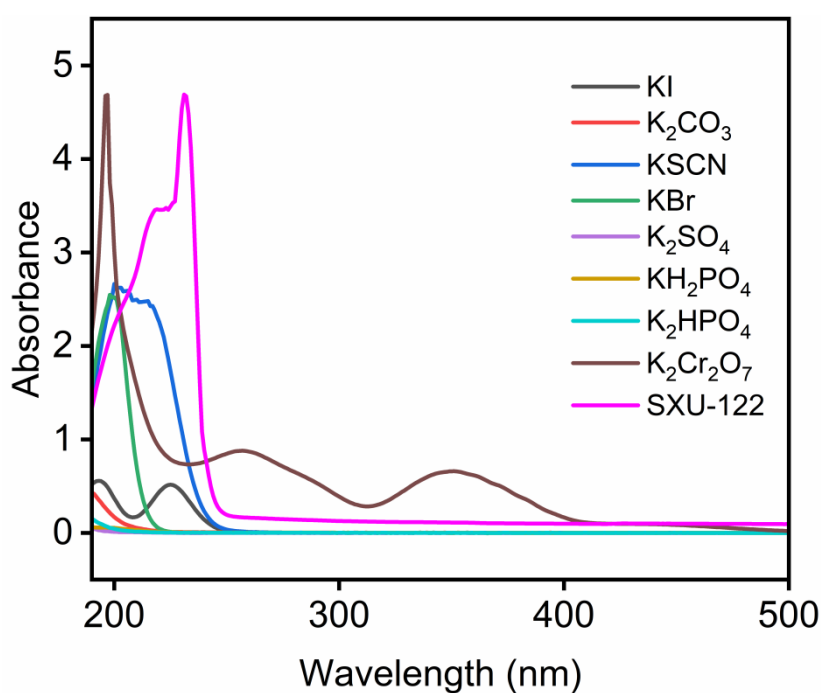


Figure S10. UV-Vis absorption spectra of different potassium salts with different anions and SXU-122 in deionized water.

Section 5 Supporting References

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