

## Supporting Information

### **Ti-based MOF nanosheets as a mass spectrometry imaging matrix for low molecular weight compounds to reveal the spatiotemporal content changes of hepatotoxic components during the processing of *Polygonum multiflorum***

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**Table S1.** The signal-to-noise ratio of different anthraquinone compounds in eight different matrices.

Matrices (S/N)	Emodin in positive-ion reflector mode	Emodin in negative-ion reflector mode	Physcion	Chrysophanol	Rhein
DHB	34.8	151.2	/	/	/
CHCA	9.7	220	/	/	/
Fe <sub>3</sub> O <sub>4</sub> @ZIF-8	54.8	5218.9	466.9	500.2	8.2
Ti-based MOF nanosheets	64.2	9919.8	1732.5	1977.5	1340.7
UiO-66-PDC	/	2438.3	379.8	671.9	/
UiO-66-(OH) <sub>2</sub>	9.1	2534.7	592.6	618.1	467
UiO-66-GA	/	3711.2	490.4	571.7	29.4
MIL-101(Cr)	6.8	7.9	21.6	19	/

**Table S2.** The coefficient of variation (CV) of signal intensity for parallel points or different sub regions within a point

CV(%)	Fe <sub>3</sub> O <sub>4</sub> @ZIF-8	Ti-based MOF nanosheets	UiO-66-PDC	UiO-66-(OH) <sub>2</sub>	UiO-66-GA	MIL-101(Cr)
Position	28.76	13.70	23.89	49.01	27.11	163.80
Spot	29.02	3.13	15.18	21.29	7.87	70.37

## EXPERIMENTAL SECTION

### 1. *Synthesis of Fe<sub>3</sub>O<sub>4</sub>@ZIF-8 MNCs*

FeCl<sub>3</sub>·6H<sub>2</sub>O (8.1 g), sodium acetate (12.0 g), Na<sub>3</sub>Cit·2H<sub>2</sub>O (2.0 g) were dissolved in ethylene glycol (200 mL). The obtained homogeneous yellow solution was transferred to autoclave, and then heated to 200 °C for 10 h. After reaction, the product was separated with a magnet and washed with water and ethanol for several times.

The Fe<sub>3</sub>O<sub>4</sub> microspheres (0.35 g) were dispersed in 20 mL of 50% ethanol solution containing 2 mmol Zn(NO<sub>3</sub>)<sub>2</sub> and 0.2 mmol HCl. Then, 40 mL of 50% ethanol solution containing 20 mmol 2-methylimidazole (HMeIM) was added to above suspension. The resulting mixture was stirred with ultrasound at room temperature for 5 min. The products were collected with a magnet and washed with ethanol and water.

### 2. *Synthesis of UiO-66*

A 20 mL vial with a screw cap loaded with anhydrous ZrCl<sub>4</sub> (0.54 mmol), concentrated HCl (1 mL), and DMF (15 mL) was sonicated until fully dissolved. BDC (0.74 mmol) was then added, and the mixture was sonicated for 10 min before being heated at 80 °C overnight. The resulting white powder sample was collected by centrifugation, successively washed with DMF (3×30 mL) and ethanol (3×30 mL), and then dried in a vacuum oven at 50 °C. UiO-66 was activated at 120 °C before further experiments.

### 3. *Synthesis of UiO-66-PDC*

Twenty-eight milligrams of UiO-66, 167 mg (1.0 mmol) of PDC, and 6 mL of methanol were added to a Teflon-capped 20 mL glass vial. The mixture was stirred at 60 °C for 24 h. After being cooled to room temperature, the resulting product was separated by centrifugation and washed with fresh methanol (20 mL, 3 times per day over 3 days) and ethanol (20 mL, 3 times per day over 3 days). Finally, the product was dried at 70 °C overnight under vacuum.

#### 4. *Synthesis of UiO-66-(OH)<sub>2</sub>*

In a typical synthesis, a 20 mL vial with a screw cap loaded with anhydrous ZrCl<sub>4</sub> (0.54 mmol), concentrated HCl (1 mL), and DMF (15 mL) was sonicated until fully dissolved. The ligand DHT (0.74 mmol) was then added, and the mixture was sonicated 10 min before being heated at 80 °C overnight. The resulting yellow powder sample was collected by centrifugation, successively washed with DMF (3×30 mL) and ethanol (3×30 mL), and then dried in a vacuum oven at 50 °C. The product was activated at 120 °C before further experiments.

#### 5. *Synthesis of UiO-66-GA*

GA (100 mg) and UiO-66 (80 mg) were successively added to deionized water (20 mL). The mixture was then allowed to stir at room temperature for 1 h. The product was collected by centrifugation and washed with deionized water and ethanol, respectively. Afterward, the above product was dried overnight at 60 °C in vacuum.

#### 6. *Synthesis of MIL-101(Cr)*

Briefly, a certain amount of reactant (H<sub>2</sub>BDC (166 mg at 1 mmol), Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (400 mg at 1 mmol), fluorhydric acid (0.2 ml at 1 mmol)) was

dissolved in ultrapure water (15 mL), and synthesized by solvothermal treatment at 220 °C for 8 h. After being cooled to room temperature, the resultant green crystalline solid was washed thoroughly with water and ethanol and collected by centrifugation.

Typically, MIL-101 was redispersed and further purified by solvothermal treatment in ethanol at 80 °C for 24 h. After, the resulting green solid was soaked in NH<sub>4</sub>F (1 M) solution at 70 °C for 24 h, then immediately filtered and washed with hot water several times, which in order to thoroughly remove the redundant reactant in the hole of MIL-101. Finally, the green solid was then evacuated in vacuum at 150 °C for 12 h to form dehydrated MIL-101.