Supplementary Information

Calix[6]arene Functionalized Lanthanide Metal-Organic Frameworks with Boosted Performance on Identifing Anti-epidemic Pharmaceutical

Lu-Dan Yu,[a] Yuan-Jun Tong,[a] Nan Li,[a] Yating Yang,[a] Pengfei Ye,[a] Gangfeng Ouyang[a,b,c] Fang Zhu*[a]

[a] MOE Key Laboratory of Bioinorganic and Synthetic Chemistry/KLGHEI of Environment and Energy Chemistry, School of Chemistry, Sun Yat-sen University, Guangzhou, 510275, China.

[b] Chemistry College, Center of Advanced Analysis and Gene Sequencing, Zhengzhou University, Kexue Avenue 100, Zhengzhou 450001.

[c] Guangdong Provincial Key Laboratory of Emergency Test for Dangerous Chemicals, Guangdong Institute of Analysis (China National Analytical Center Guangzhou), Guangdong Academy of Sciences, 100 Xianlie Middle Road, Guangzhou 510070, China.

* Corresponding Author: F. Zhu, Email: ceszhf@sysu.edu.cn

1. Supplementary Experimental Section

1.1 Materials and Reagents. Carbon Mesh was purchased from Toray Industries, Inc (Japan), $Tb(NO_3)_3 \cdot 6H_2O$, dimethylformamide (DMF), and all the other interfering compounds for *Prednis* detection experiments were purchased from Aladdin Reagent (Shanghai, China). All suspensions were prepared using ultrapure water (18.2 MΩ cm) from a Millipore Direct-Q system.

1.2 Apparatus. The UV-vis spectra were collected on an UV-2450 spectrophotometer (Shimadzu, Japan). Quanta 200 scanning electron microscopy (SEM, U.S.A.) was used to characterize the sizes and morphology. Fourier transform infrared (FT-IR) spectra were obtained using a Nicolet 5700 FT-IR spectrometer. Fluorescence spectra were performed on an F-97 Pro fluorescence spectrometer. The excitation wavelength, slit widths (including excitation and emission), and the photomultiplier tube (PMT) voltage were set at 290 nm, 10 nm and 650 V, respectively. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on powders with a Thermo ESCALAB 250 spectrometer using an Al Ka monochromator source (*hv*=1486.6 eV) and a multidetection analyzer.

1.3 Synthesis of Tb-BTC MOF and structurally modification of TB-Cx[6]. Tb-BTC was synthesized in a relatively mild way according to the method in the literature with a slight adjustment [1]. 1 g of $Tb(NO_3)_3 \cdot 6H_2O$ powder was mixed with 0.5 g of BTC and dissolved in 54 ml DMF mixed with 4 ml water. After stirring for 1 h, the mixture was treated at 100 °C for 12 h to obtain Tb-BTC suspension in DMF with underreacted ligands BTC and Tb metal ions The mixture suspension above was centrifuged and washed by DMF, water and ethanol, respectively. Finally, the white powder of Tb-BTC was got from drying in vacuum oven at room temperature. The structure modification route of Tb-BTC was according to a literature procedure in which 100 mg of the Tb-BTC powder and 50 mg Cx[6] were mixed in 10 ml methylbenzene within a glass bottle and took sonication for 1 h and left standing overnight. The solutions were filtered to get rid of parent solids. The solutions were dried at 150°C for 24 h under vacuum to obtain the final product TB-Cx[6] powder.

1.4 Quantification determination of *Prednis* with TB-Cx[6] fluorescence probe. Firstly, the TB-Cx[6] stock suspension was prepared by mixing 5 mg TB-Cx[6] to 5 mL ultrapure water under sonication for 3 min. Subsequently, the TB-Cx[6] suspension (50 μL) was respectively mixed with an aliquot of 200 μL different concentrations of *Prednis* methanol solutions. The mixture above was diluted with ultrapure water to control the total volume 2000 μL. The fluorescence spectra were measured with the excitation wavelength at 290 nm. The Tb^{3+} fluorescence peak at 545 nm was measured for quantification.

1.5 Selectivity of the assay to *Prednis*. To assess the sensing selectivity of the TB-Cx[6] system for *Prednis*, potential interfering metal ions and were used to investigate the specificity of the *Prednis* assay under identical conditions. The concentration of *Prednis* is set at 100 ng/mL, and the level of other analytes is 5 folds than *Prednis*. The interference of other analytes is quite tiny, indicating that this fluorescence probe has high sensitivity and selectivity. It is worth noting that bare Tb-BTC for *Prednis* detection were disturbed by lots of analytes. This is due to the selective and efficient enrichment of *Prednis* into the solid material by Cx[6].

1.6 Analysis of *Prednis* in real water samples. To test the general applicability of TB-Cx[6] probe, standard addition method was performed on the water samples (river water and sea water) for our assay. Real samples of the Pearl River water were filtered through the 0.22 μm cellulose acetate filters to remove insoluble impurities that may exist in the water. Subsequently, 350 μL of the obtained water samples and 100 μL of TB-Cx[6] probe were diluted to 700 μL with deionized water. Subsequently, the mixture was used for performing fluorescent and L-MS measurements. The concentrations of *Prednis* in the tested water samples are presented in Table S1.

1.7 Preparation of TF. Firstly, the 20 mg solid TB-Cx[6] was added into 10 mL hexamethylene and then sonicated to around 30 mins. Then 40 mg PDMS was added into the above mixture. The mixed solution was strongly stirred and sonicated to obtain the suspension of TB-Cx[6]. Subsequently, a cleaned carbon mesh was fixed on the coating instrument (Figure S10) and the obtained TB-Cx[6] suspension was gradually dropped onto the carbon mesh surface. A round push rod rolls on the TF film to control the thickness and uniformity of the coating. Finally, the TF was obtained and dried for 30min at 85 °C under vacuum.

1.8 Design of the TF equipped drone water sampler. A drone of with automatic return function was purchased from Dajiang (Mavic Mini-DJI, Shenzhen, China). This drone was tested to have an additional lift capacity of 200 g and a flight range of 3000 m. The TB-Cx[6] TFs were fixed to the lower part of the buoyancy stents by clamps. The TB-Cx[6] TFs were all immersed into the water to a depth about 10 cm, when the drone was floating on water.

1.9 Analysis of *Prednis* by TF. As the universality and particularity of Prednis, as well as the uncertainty of nocuity in real samples, TFME drone water sampler was fabricated and used to analysis Pearl River Water. Two TB-Cx[6] membranes were equipped onto the drone sampler. The drone was then lifted off from a stent placed on the deck and flown toward real-water. After touching down on the surface of the water the membranes were all immersed into the water by gravity. The drone was then allowed to sit on the surface of the water for 10 min of sampling. After sampling, the TF is taken out and dried, and then the fluorescence test is performed. The concentrations of *Prednis* in the tested real water is presented in Table S2.

75

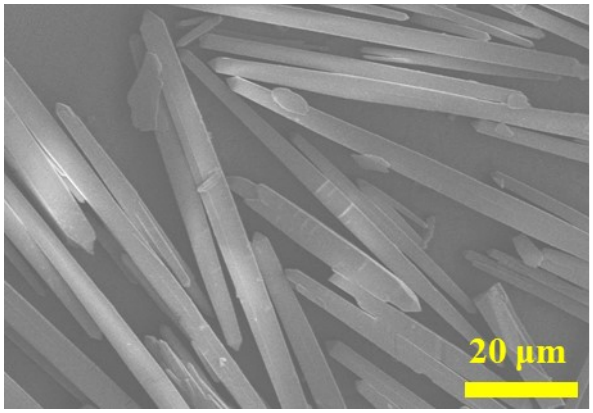


Figure S1. SEM image of bare Tb-BTC MOF

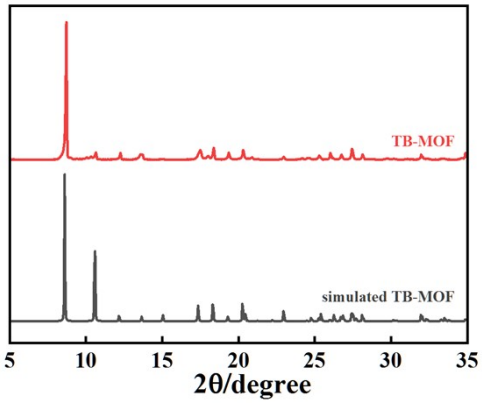


Figure S2. XRD pattern of TB-MOF and simulated TB-MOF

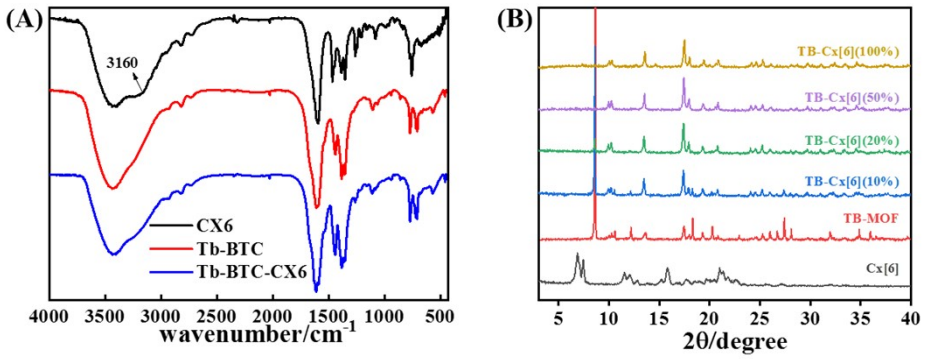


Figure S3. (A) FTIR and (B)XRD spectra of Cx[6], Tb-BTC and TB-Cx[6] adding different amounts of Cx[6], respectively

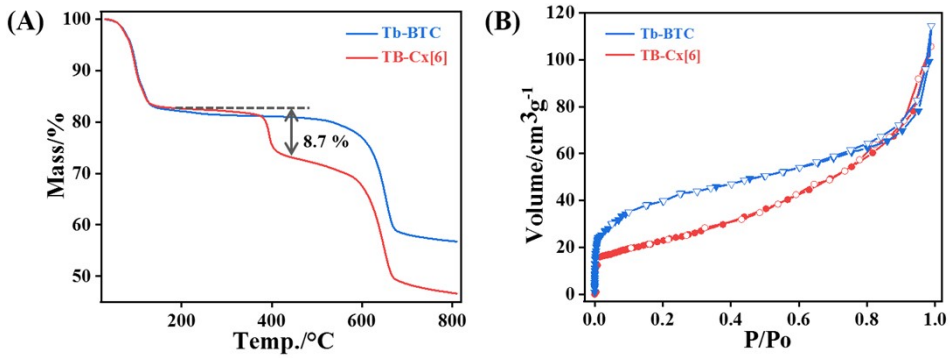


Figure S4. (A) TGA curves and (B) BET pattern of Tb-BTC and TB-Cx[6]. The TGA was performed at temperature ranged 30 to 800 ℃, heating rate was 10℃/min, and the atmosphere is nitrogen.

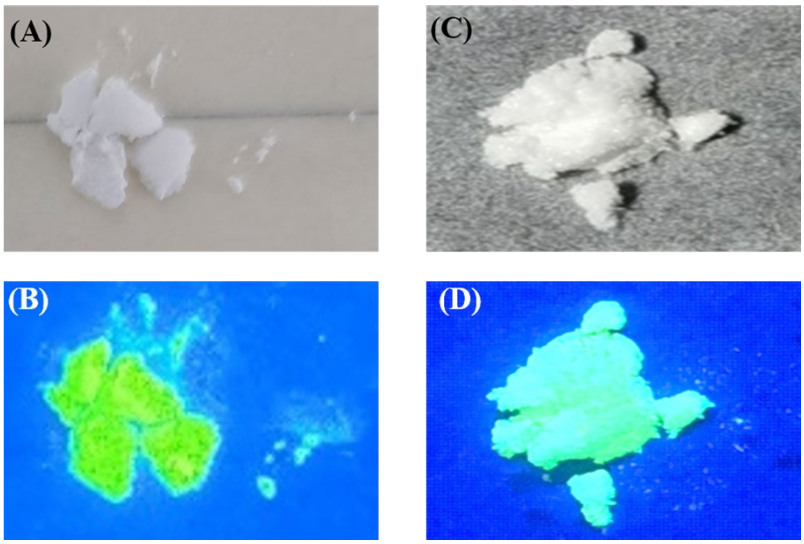


Figure S5. Photos of Tb-BTC under (A) sunlight and (B) UV light (254 nm). Photos of TB- Cx[6] under (C) sunlight and (D) UV light (254 nm)

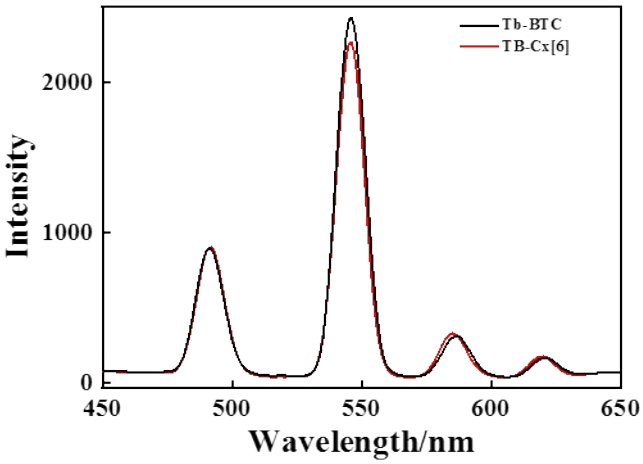
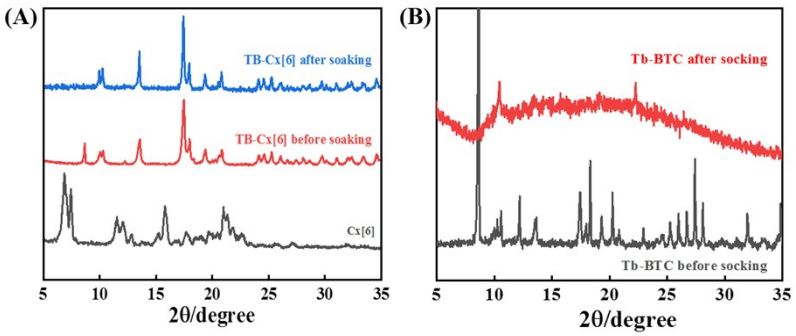


Figure S6. Fluorescent spectra of Tb-BTC and TB- Cx[6].



105

106

107 **Figure S7.** XRD pattern of TB- Cx[6] (A) and Tb-BTC (B) before and after soaking in water for 15 days.

108

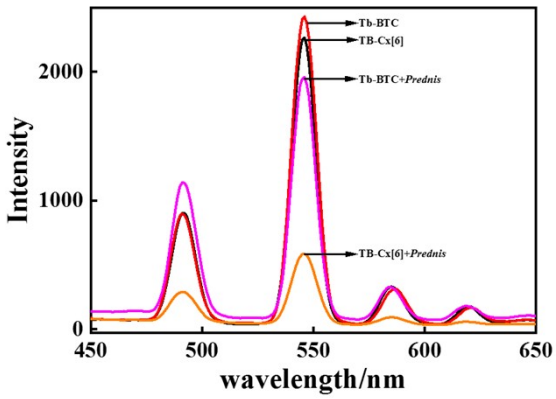


Figure S8. Fluorescence spectra of Tb-BTC, TB- Cx[6], Tb-BTC and TB- Cx[6] with 1000 ng/mL *Prednis* respectively.

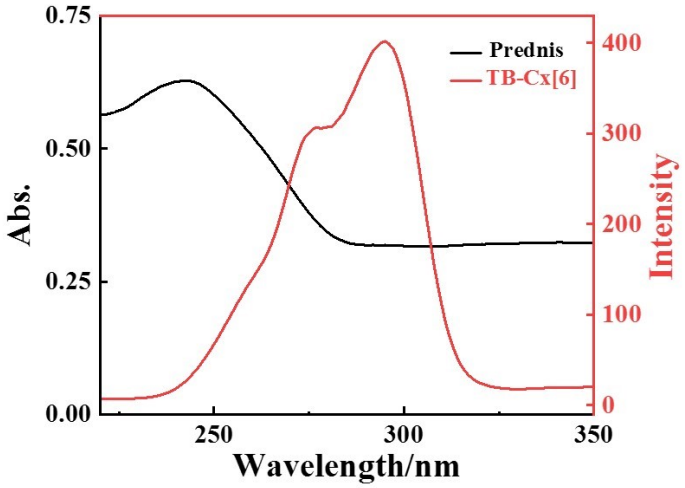


Figure S9 Ultraviolet absorption spectrum of *Prednis* and fluorescence emission spectrum of TB-Cx[6].

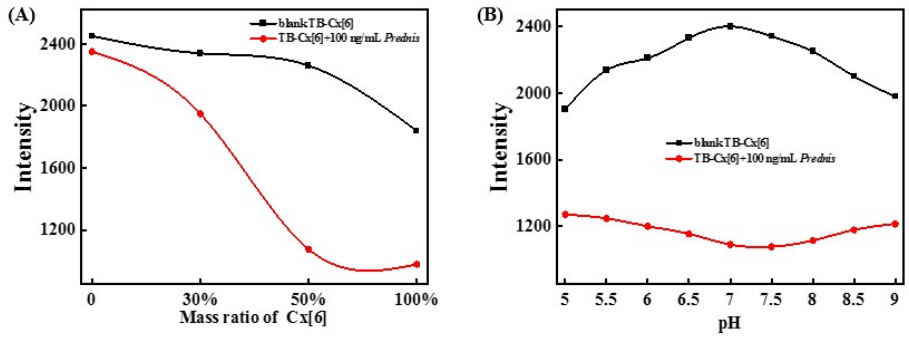


Figure S10. (A) Effects of Cx[6] contents for *Prednis* analysis. (B) Effects of different pH before and after addition of 1000 ng/mL *Prednis*.

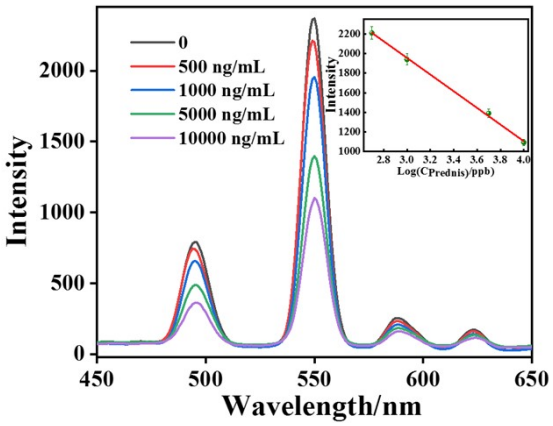


Figure S11 Fluorescence intensity curves of the Tb-BTC MOF fluorescent probe with different concentrations of *Prednis*.

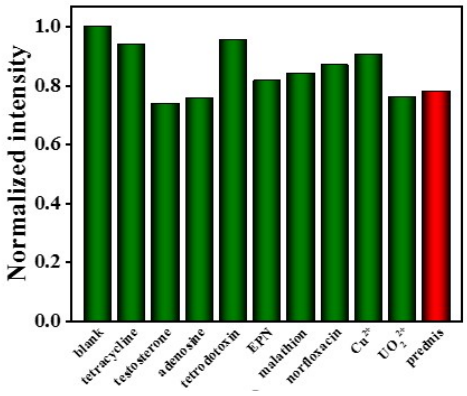


Figure S12. Selectivity assay of Tb-BTC to *Prednis* in the presence of various interfering species (tetracycline, tetrodotoxin, adenosine, 2-deoxyadenosine(EPN), malathion, norfloxacin, Cu^{2+} and UO_2^{2+}). The concentration of *Prednis* was 100 ng/mL, the concentration of each interfering species was 5 times of *Prednis*.

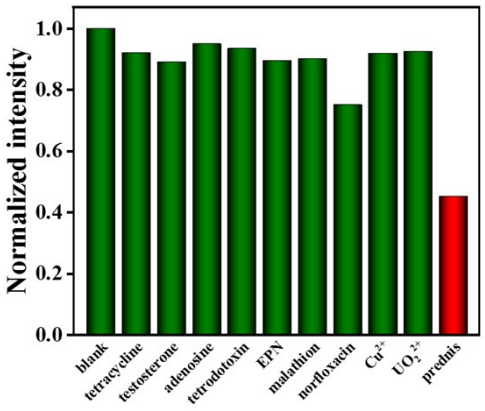


Figure S13. Selectivity assay of TB-Cx[6] to *Prednis* in the presence of various interfering species (tetracycline, tetrodotoxin, adenosine, 2-deoxyadenosine(EPN), malathion, norfloxacin, Cu^{2+} and UO_2^{2+}). The concentration of *Prednis* was 100 ng/mL, the concentration of each interfering species was 5 times of *Prednis*.

134

135 **Figure S14.** Coating machine for making TF.

136

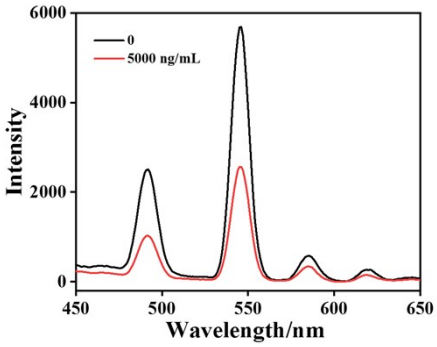


Figure S15. The spectra of TB-Cx[6] thin film after immersed into simulated sea water with different concentration of *Prednis*

Table S1. Detection *Prednis* in Pearl river water samples by using TB-Cx[6], TF and LC-MS.

methods	Spiked (ng/mL)	Detected (ng/mL)	Recovery (%)	RSD (n=5)	LC-MS (ng/mL)	Consistency (%)
TB-Cx[6]	0	ND	-	6.7%	-	-
	10.0	11.4	114.0	8.1%	10.7	106.5
	50.0	51.7	103.4	5.9%	50.9	101.5
TF	0	ND	-	6.5%	-	-
	10.0	11.8	118.0	7.8%	10.7	110.3
	50.0	52.7	105.4	5.3%	50.9	103.5

ND indicated not detected. Consistency $=C_{Fluorescence} / C_{(LC\text{-}MS)}$ 100%

Table S2. Detection *Prednis* in simulated sea water[a] by using TF.

methods	Spiked (ng/mL)	Detected (ng/mL)	Recovery (%)	RSD (n=3)	LC-MS (ng/mL)	Consistency (%)
TF	5000.0	5397	108.0	7.4%	5242	103.0

a: Simulated seawater was prepared in accord with the main constituents of real seawater as specified in Table S3 (China Petroleum Processing and Petrochemical Technology, 2022, 24, 91-100).

149 **Table S3.** Main constituents of simulated seawater as used in the study

Main component	Percentage salt (%)	Concentration (g/L)
NaCl	77.76	27.2
$MgCl_2$	10.88	3.80
$MgSO_4$	4.38	1.70
$CaSO_4$	3.60	1.20
K_2SO_4	2.47	0.90
$CaCO_3$	0.35	0.10

150