

Supporting Information

Fluorescent wearable platform for sweat Cl⁻ analysis and logic smart-device fabrication based on color adjustable lanthanide MOFs

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Experimental Section

Materials and reagents

ZrCl₄ was purchased from Admams. The ligands 2,2'-bipyridine-5,5'-dicarboxylic acid (H₂bpydc) and biphenyl-4,4'-dicarboxylic acid (H₂bpdc) were purchased from Aldrich. Europium chlorides (EuCl₃·6H₂O) and terbium nitrate (Tb(NO₃)₃·6H₂O) were prepared by dissolving their oxides in excess hydrochloric acid or nitric acid followed by evaporation and crystallization. All the other starting materials were obtained from commercial sources and used without further purification.

Preparation of UiO-67

The UiO-67 was synthesized based on the previous report with slight modifications. Typically, ZrCl₄ (0.233 g, 1 mM), H₂bpydc (0.248 g, 1 mM) and glacial acetic acid (2 g, 33.33 mM) were ultrasonically dispersed in a 100 mL Teflon-lined stainless steel container containing 60 mL N,N-dimethylformamide (DMF). The mixture was heated at 120 °C for 24 h. When cooling to room temperature naturally, white solid was harvested by centrifugation (12000 rpm, 3 min) and washed with DMF. Then the product was washed with methanol via Soxhlet extraction for 24 h to remove organic species encapsulated within the pores.

Preparation of Eu³⁺@UiO-67

Eu³⁺@UiO-67 was prepared by immersing the UiO-67 solid (50 mg) in 20 mL ethanol solutions of chloride salts of Eu³⁺ (10 mM) at 25 °C for 24 h. Then the resulting solid were collected by centrifugation, washed with ethanol to remove the excessive and physical absorbed Eu³⁺, and dried at 60 °C under vacuum.

Preparation of Ag⁺/Eu³⁺@UiO-67

Ag⁺/Eu³⁺@UiO-67 was prepared by immersing above Eu³⁺@UiO-67 solid (30 mg) in 20 mL aqueous solution of Ag⁺ (0.5 M) at room temperature for 1 h. Then the resulting products were separated by centrifugation, washed with water, and dried under vacuum.

Preparation of DUT-101

DUT-101 were prepared by using a modified procedure from the literature. Tb(NO₃)₃·6H₂O (0.09 g, 0.2 mM) and H₂bpdc (0.121 g, 0.5 mM) were mixed in 12 mL H₂O/DMF (1:4) and stirred for 60 min under ambient conditions. The resulting solution was transferred to a 25 mL Teflon-lined stainless-steel container and heated at 140 °C for 72 h. After cooling to room temperature, the colorless solid was collected by filtration, washed with ethanol and dried in air.

Fabrication of wearable sensor device

Ag⁺/Eu³⁺@UiO-67 and DUT-101 were added in an ethanol solution (10 mL) under ultrasonication. The mass ratio for Ag⁺/Eu³⁺@UiO-67 and DUT-101 adjusts to be 5, 10 and 20. Afterward, a piece of purchased cotton (1 cm x 1 cm) was immersed in the resultant solution followed by stirring for 30 min. After it was rinsed with ethanol and dried at 80 °C, the sensing cotton was acquired. The epidermal evaluation on human subjects was conducted by placing the cotton on waterproof bandage. The weight of cotton piece before and after absorption was recorded for calculating the weight gain as illustrated as the following equation:

$$\text{Weight gain (\%)} = (M_1 - M_0) / M_0 \times 100\%$$

Where M_1 and M_0 were the weight of cotton piece after and before load sensing materials.

Procedure of Cl^- monitoring

(1) MOFs power test: the as-prepared MOFs power ($\text{Ag}^+/\text{Eu}^{3+}@$ UiO-67 and DUT-101, 3 mg) was dispersed into the aqueous solution of Cl^- (3 mL, 100 mM). Then the suspension were vibrated and mixed to form homogeneous solution for fluorescence measurements; (2) wearable device test: the sensing performance of the cotton piece sensor was evaluated first in artificial sweat. The fluorescence response was measured after adding dropwise Cl^- (1 mL, 100 mM) to the cotton piece. The selectivity was examined by measuring the response to 1 mM in the presence of relevant species in sweat: Ca^{2+} : 3 mM, Mg^{2+} : 1 mM, Na^+ : 100 mM, K^+ : 24 mM, NH_4^+ : 8 mM, lactate: 60 mM, urea: 6 mM. The on-body evaluation of sweat $[\text{Cl}^-]$ was performed in compliance with the protocol that was approved by the institutional review board (IRB) at the University of California. Tests were performed on one subjects: subject 1, male, age = 27, height = 178 cm and weight = 77 kg, while running indoor for about 1 h. The subject was healthy with no prior history of heart conditions, diabetes, or chronic skeletal muscular pain. In addition, the subject gave written, informed consent before participating in the test. In the experiments, the wearable sensors were placed on the subjects arm and back and fluorescence measurement was recorded every 10 min. The indoor temperature and humidity were 28 °C and 55%.

The LOD of Cl^- was evaluated by the following equations:

$$S_b = \sqrt{\frac{\sum (I_0 - I_1)^2}{N - 1}}$$

$$\text{LOD} = 3S_b/S$$

Where S_b is the standard deviation for replicating detections of blank solutions ($N=20$); I_0 is the fluorescence intensity of I_{614}/I_{545} in artificial sweat without Cl^- ; I_1 is the average of I_0 ; S is the slope of the linear fitted curve in Fig. 4f

Characterizations

PXRD patterns were recorded on a Bruker D8 Focus diffractometer with $\text{Cu K}\alpha$ radiation under 40 kV and 40 mA. TEM was carried out on a JEOL JEM-2010F electron microscope operated at 200 kV. SEM images were recorded with a HitachiS-4800 equipped with an energy dispersive X-ray spectrometer (EDS) with a cold field emission gun operating at 2 kV and 10 μA . UV-vis absorption spectra were measured with an Agilent 8483 UV-vis spectrometer. Nitrogen adsorption-desorption isotherms were measured using a Tristar 3020 analyzer at the liquid nitrogen temperature. Surface areas were calculated by the BET method. The measurement of metal ion concentration was performed on Perkin Elmer 8300 ICP-OES. XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with $\text{Mg K}\alpha$ radiation ($h\nu = 1253.6$ eV). Luminescence excitation and emission spectra of the samples were obtained on an Edinburgh FLS920 spectrophotometer. Lifetime measurements were performed on an Edinburgh FLS920 phosphorimeter using a 450 W xenon lamp as excitation source. The absolute external luminescent quantum efficiency was determined employing an integrating sphere (150 mm diameter, BaSO_4 coating) from an Edinburgh FLS920 phosphorim.

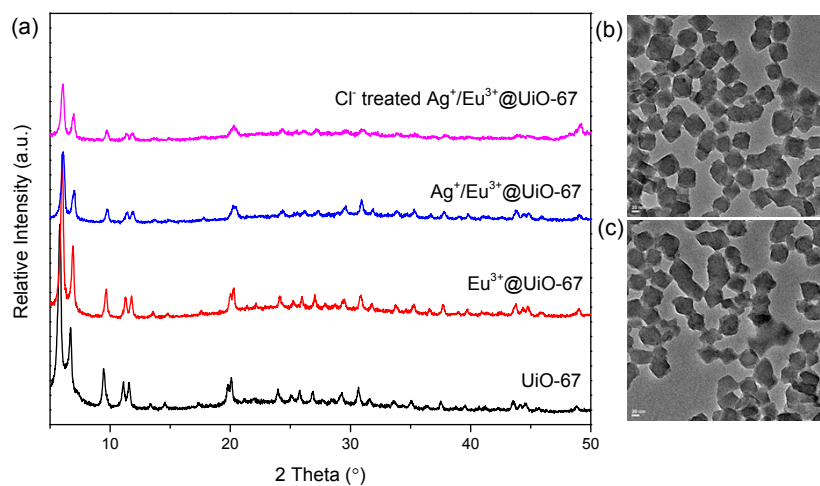


Fig. S1 (a) PXRD patterns of $\text{Eu}^{3+}@UiO-67$, $\text{Ag}^+/\text{Eu}^{3+}@UiO-67$ and Cl^- treated $\text{Ag}^+/\text{Eu}^{3+}@UiO-67$ and TEM images of $\text{Eu}^{3+}@UiO-67$ (b) and $\text{Ag}^+/\text{Eu}^{3+}@UiO-67$ (c). The scale in (b) and (c) is 20 nm.

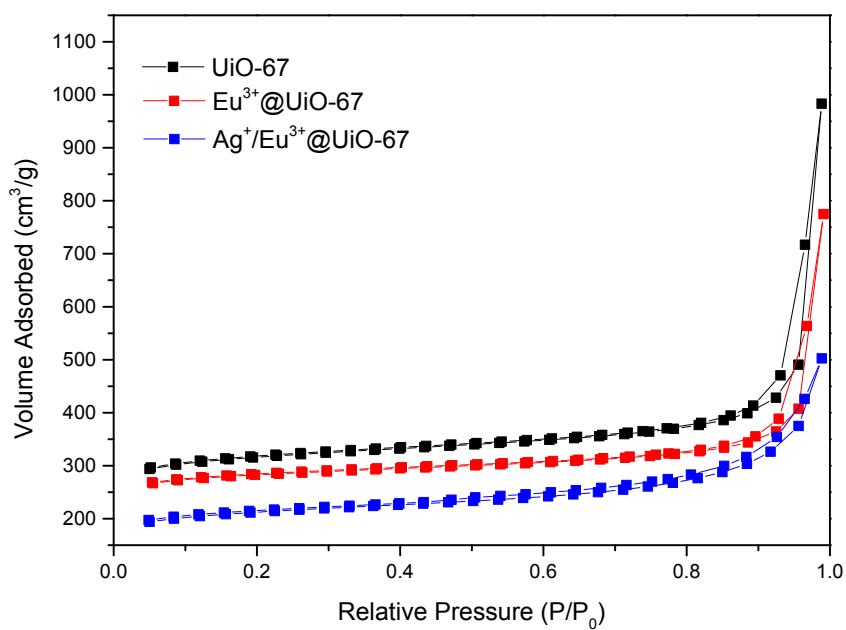


Fig. S2 N_2 adsorption-desorption isotherms of $UiO-67$, $\text{Eu}^{3+}@UiO-67$ and $\text{Ag}^+/\text{Eu}^{3+}@UiO-67$.

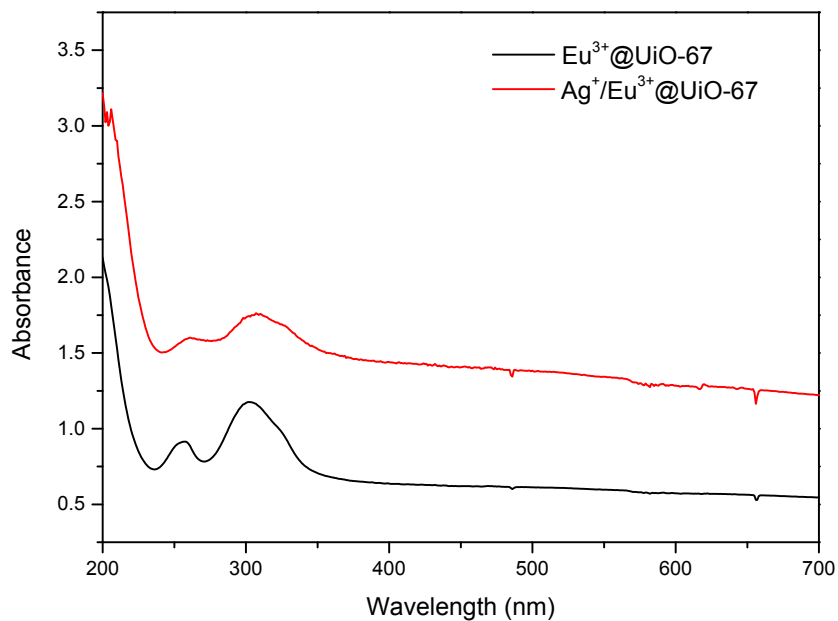


Fig. S3 UV-Vis absorption spectra of suspended $\text{Eu}^{3+}@UiO-67$ and $\text{Ag}^+/\text{Eu}^{3+}@UiO-67$ in aqueous solution.

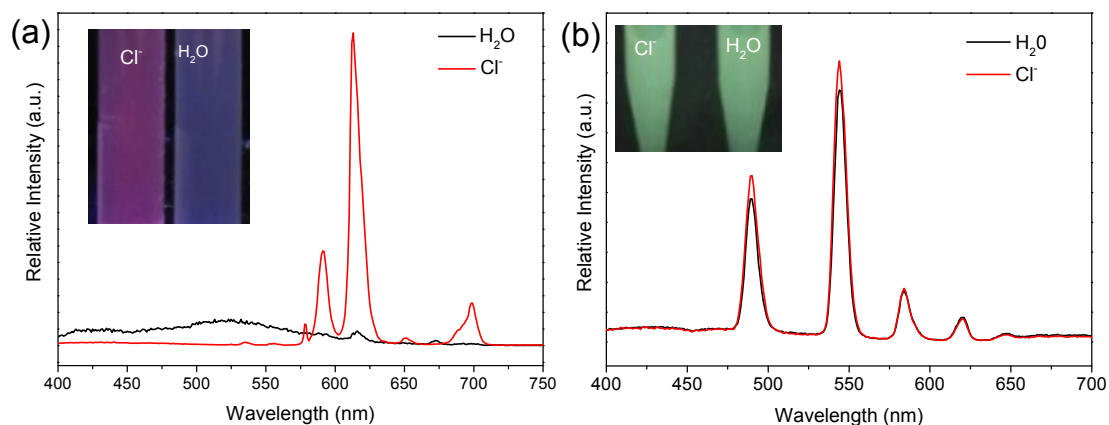


Fig. S4 Fluorescence response of $\text{Ag}^+/\text{Eu}^{3+}@UiO-67$, $\lambda_{\text{ex}} = 334 \text{ nm}$ (a) and DUT-101, $\lambda_{\text{ex}} = 314 \text{ nm}$ (b) towards Cl^- (100 mM) in water. The insets give corresponding fluorescence photographs under UV-light irradiation of 365 nm.

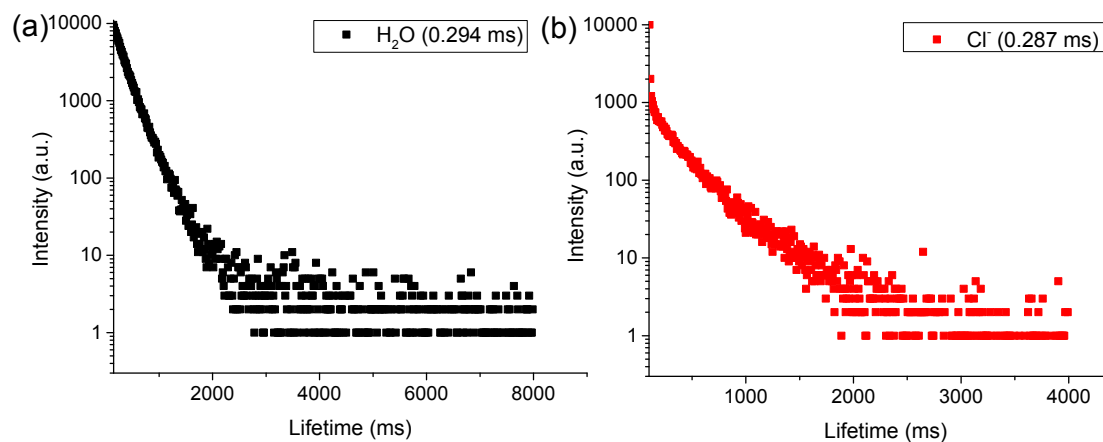


Fig. S5 Decay curves of Eu³⁺@UiO-67 suspension in water (a) and Ag⁺/Eu³⁺@UiO-67 suspension in presence of Cl⁻ (100 mM). The excitation wavelength is 334 nm.

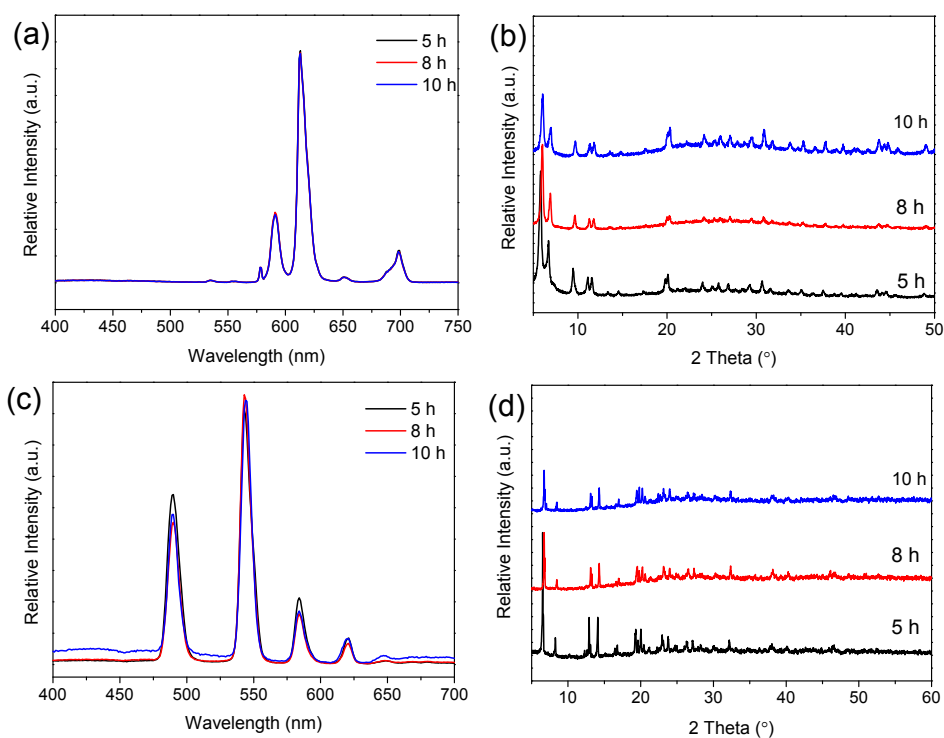


Fig. S6 Hour-to-hour fluorescence stability (a) and structure stability (b) of Eu³⁺@UiO-67 in water under excitation at 334 nm and hour-to-hour fluorescence stability (c) and structure stability (d) of DUT-101 under excitation at 314 nm.

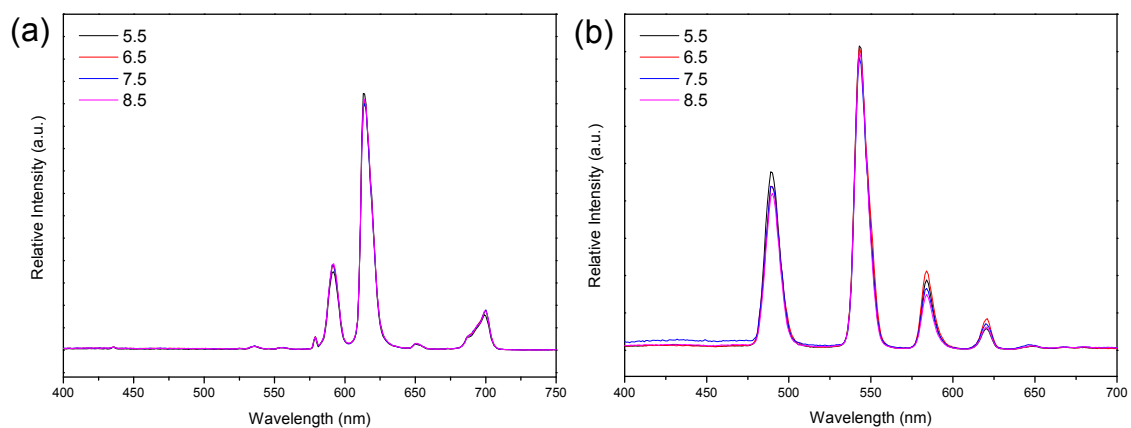


Fig. S7 pH fluorescence stability of Eu³⁺@UiO-67 (a) and DUT-101 (b)

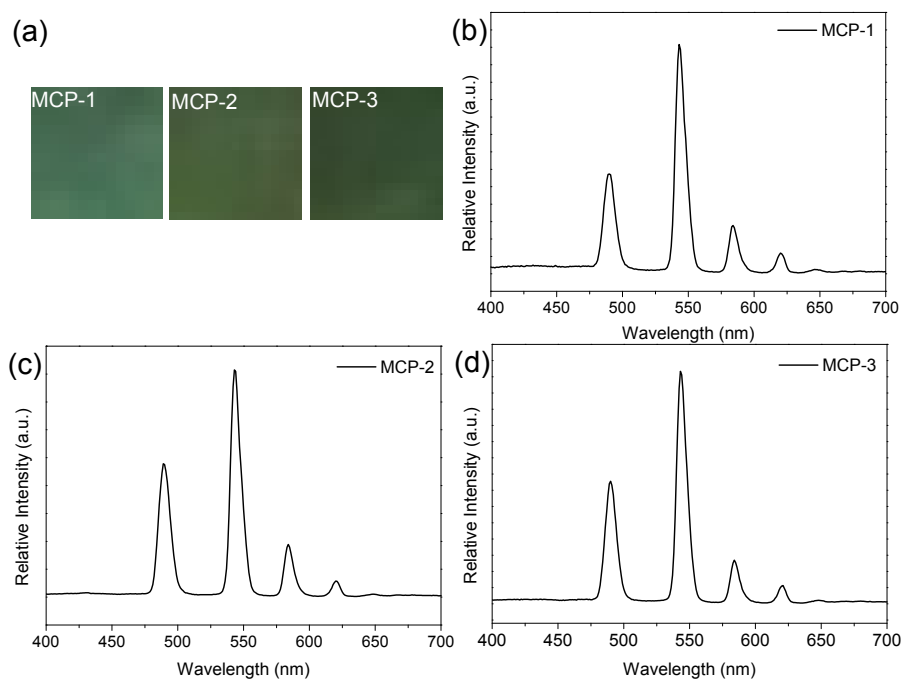


Fig. S8 The corresponding fluorescence photographs of MCP-1, MCP-2 and MCP-3 under 365 nm UV-light (a) and emission spectra of MCP-1 (b), MCP-2 (c) and MCP-3 (d), $\lambda_{\text{ex}} = 365$ nm.

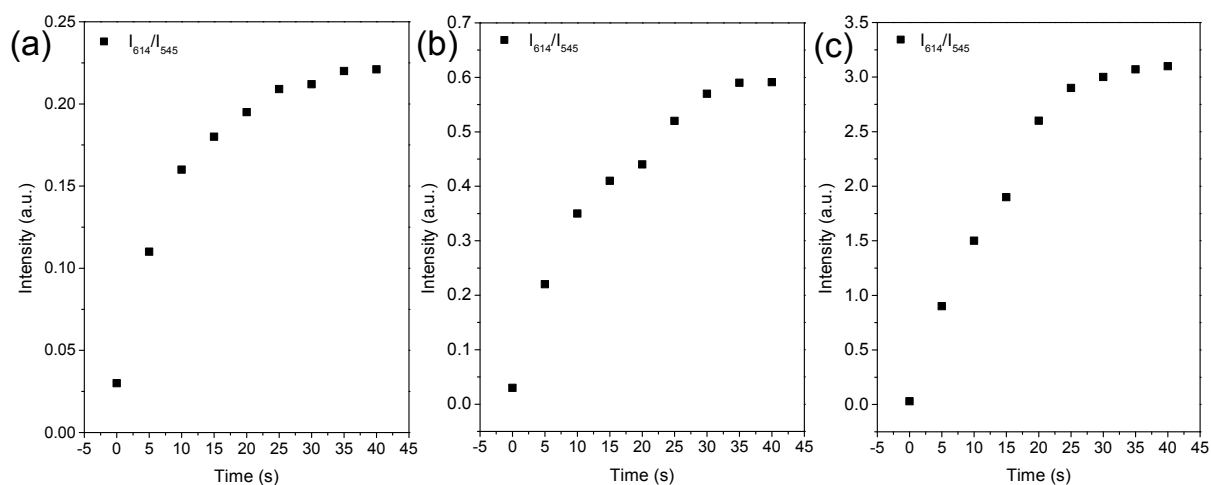


Fig. S9 Fluorescence response of MCP-1 (a), MCP-2 (b) and MCP-3 (c) towards Cl^- (1 mL, 100 mM) aqueous solution within 40 s, $\lambda_{\text{ex}} = 365 \text{ nm}$.

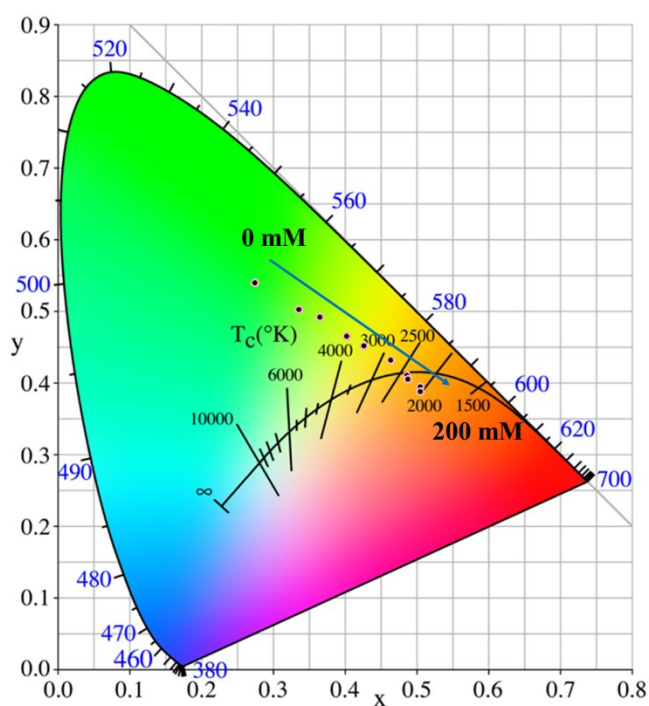


Fig. S10 The CIE chromaticity coordinate of MOFs loading cotton piece calculated from the emission spectra shown in Fig. 3e, which shows the fluorescence color change with Cl^- concentration (0-200 mM).

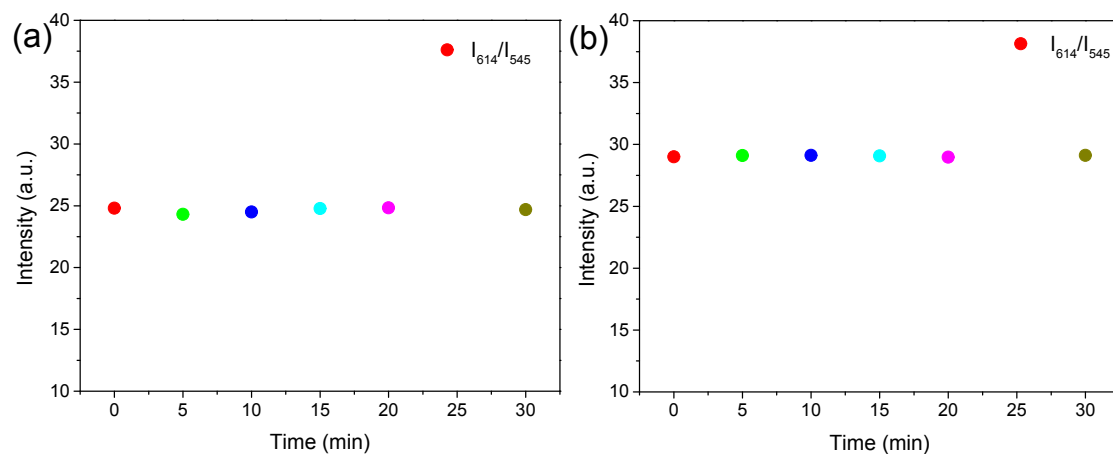


Fig. S11 Fluorescence response of the wearable device towards detached time from the two locations: arm (a) and back (b) within 30 min for 10 min running, $\lambda_{\text{ex}} = 365$ nm.

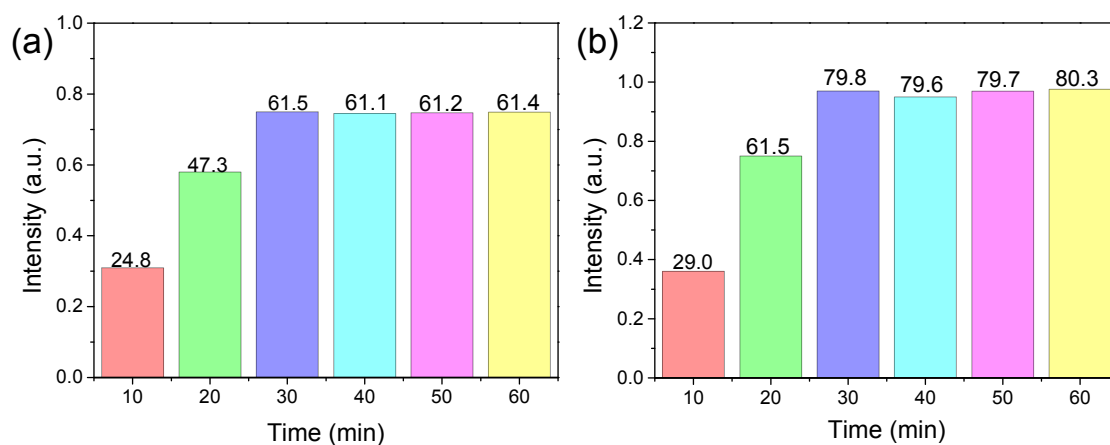


Fig. S12 Off-body monitoring from collected sweat samples by the wearable device on different location: arm (a) and back (b) within 1 h running, the insets show the corresponding Cl^- level (mM) every 10 min, $\lambda_{\text{ex}} = 365$ nm.