

Supplementary Information (SI) for ChemComm.  
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## Supporting Information

### **UiO-66-derived nano-separation microelectrode for in vivo dopamine sensing with high sensitivity and selectivity**

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## 1. Experimental Procedures

### 1.1 Reagents and solutions

Zirconium (IV) chloride and Pyromellitic Acid were purchased from Meryer (Shanghai, China). Tricarbonylchloro (glycinato) ruthenium (II) (CORM-3) was purchased from Aladdin (Shanghai, China). XC72 carbon was purchased from Sinero (Suzhou, China). ascorbate (AA) and dopamine (DA) were purchased from Sigma (St Louis, MO, USA). 3,4-Dihydroxyphenylacetic acid (DOPAC), uric acid (UA), and serotonin hydrochloride (5-HT) were purchased from Alfa Aesar. norepinephrine (NE) was purchased from OriLeaf (Shanghai, China). Epinephrine (EP) was purchased from Psaitong (Beijing, China). NaCl, KCl, MgCl<sub>2</sub>, NaHCO<sub>3</sub>, KH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub> were purchased from Beijing Chemical Corporation (Beijing, China). Artificial cerebrospinal fluid (aCSF) was prepared by dissolving NaCl (126 mM), KCl (2.50 mM), KH<sub>2</sub>PO<sub>4</sub> (1.25 mM), MgCl<sub>2</sub> (1.20 mM), NaHCO<sub>3</sub> (26.0 mM), and CaCl<sub>2</sub> (1.20 mM) into Milli-Q water, and the solution pH was adjusted to 7.4. Unless otherwise specified, all experiments were performed at room temperature (~25 °C).

### 1.2 Apparatus and measurements

Electrochemical measurements were performed on an electrochemical analyzer (CHI 1040C, Shanghai, China) with a three-electrode system. Microsized Ag/AgCl microelectrode is used as reference electrode, and Pt wire were used as counter electrode (only for amperometric method), UiO-66-(COOH)<sub>2</sub>/XC72/CFE, UiO-66-(COOH)<sub>2</sub>/CFE, XC72/CFE and CFE were used as working electrode. aCSF (pH 7.4) was used as the electrolyte. Scanning electron microscopy (SEM; Hitachi SU8010, Japan) was used for characterizing UiO-66-(COOH)<sub>2</sub>, XC72, CFs, UiO-66-(COOH)<sub>2</sub>/XC72/CFs. Elemental analysis of the UiO-66-(COOH)<sub>2</sub> was conducted using energy-dispersive X-ray spectroscopy (EDS, BRUKER, Germany). XPS were recorded on a Thermo ESCALAB 250. X-ray diffraction (XRD) data were obtained on a SHIMADZU XRD-7000 X-Ray diffractometer operating in the 2θ = 3-80° range (10.0°/min). Surface area was measured using the Brunauer-Emmett-Teller (BET) method with a Belsorp-Mini II system. The FT-IR spectra were detected in SHIMADZU IRPrestige-21 FT-IR

spectrometer.

### **1.3 Synthesis of UiO-66-(COOH)<sub>2</sub>**

UiO-66-(COOH)<sub>2</sub> was prepared via a solvothermal method under a refluxing process.<sup>1</sup> 1,2,4,5-benzenetetracarboxylic acid (3.33 mmol) and zirconium tetrachloride (3.47 mmol) were sequentially added into a round-bottom flask containing 20 mL of water. After mixing, 13.3 mL of acetic acid was added and the mixture was stirred for 20 min until the solution became transparent. The resulting mixture was refluxed at 100 °C for 24 h, and a white precipitate was generated. Then the solid product was collected by centrifugation and dispersed in methanol for 3 d with continuous stirring. Subsequently, the sample was activated under vacuum drying at 120 °C for 3 h to obtain UiO-66-(COOH)<sub>2</sub> sample.

### **1.4 Preparation of Carbon Fiber Microelectrodes**

Carbon fiber microelectrode (CFE) was prepared as reported previously.<sup>2, 3</sup> The shell of the CFE consists of a tapered glass capillary with an opening at the tip. A glass capillary (i.d.1.5 mm, length 10 cm) was pulled into two capillaries on a microelectrode puller (PC-100, Narishige, Tokyo, Japan). The appropriate length of carbon fiber (Tokai Carbon Co., Tokai, Japan) and conductive copper wire were tightly bonded by conductive silver glue. After the conductive silver glue was solidified, the copper wire bonded with carbon fiber was passed through the conical capillary with the tip opening prepared above, so that the carbon fiber was exposed at the thin opening end of the capillary and the copper wire was exposed at the other end of the capillary. Both open ends of the capillary were sealed with cyanoacrylate. After that, the CFEs were dried at room temperature for 2 h and the length of CFE was cut into 300-500 μm under microscope, then the CFE was soaked in acetone for 10 s, followed by thoroughly rinsed with Milli-Q water. Before use, the CFE was subjected to electrochemical activation at +1.50 V (vs. Ag/AgCl) for 80 s, and then processed in 0.1 M NaOH electrolyte (0-1.0 V) at 50 mV s<sup>-1</sup> by cyclic voltammetry until a stable voltammogram was obtained. The buffers were thoroughly purged with pure nitrogen before experiments.

## 1.5 Fabrication of the UiO-66-(COOH)<sub>2</sub>/XC72/CFE

5.0 mg of the XC72 were dispersed in 5 mL Milli-Q water followed by sonication for 30 min. CFE was immersed in the XC72 solution for 6 h. The XC72/CFE was obtained after the microelectrode was dried at room temperature for 12 h. 10 mg UiO-66-(COOH)<sub>2</sub> was dissolved in 1.0 mL of Milli-Q water followed by sonication for 1 h. The XC72/CFE was then immersed in a UiO-66-(COOH)<sub>2</sub> droplet and gently rotated until the tip of the XC72/CFE fiber is completely covered by UiO-66-(COOH)<sub>2</sub>. The UiO-66-(COOH)<sub>2</sub>/XC72/CFE was obtained after the microelectrode was dried at room temperature for 12 h.

## 1.6 In vivo experiments

All animal procedures were in accordance with the guide for the care and use of laboratory animals from Chinese Ministry of Health and approved by the Animal Care and Use Committee of Beijing Normal University (No. IACUC(BNU)-NKLCNL2024-13). Adult male Sprague-Dawley rats aged 6 weeks (Charles River Laboratories, China) were kept in a 12:12 h light/dark cycle environment at ~25°C, with food and water provided ad libitum. Rats were anesthetized with isoflurane (4% induction, 2% maintenance) through a R520 gas pump (RWD, China). Body temperature was maintained at 37°C with a regulated heating blanket. Rats were secured in a stereotactic apparatus (RWD, China) throughout the procedure.<sup>4,5</sup> A skin incision was made to expose the skull. The as-prepared microelectrode was implanted (left) into striatum (Anteroposterior (AP): 0.2 mm, mediolateral (ML): 3 mm, and dorsoventral (DV): 3.5 mm from dura). using standard stereotaxic procedures. The counter electrode and micro-sized Ag/AgCl electrode were implanted into the dura of the brain. For local injection, a stainless tube was implanted into the same depth of the UiO-66-(COOH)<sub>2</sub>/XC72/CFE and keep the distance about 500 μm from each other. All local microinjection was performed at 4.0 μL·min<sup>-1</sup>.

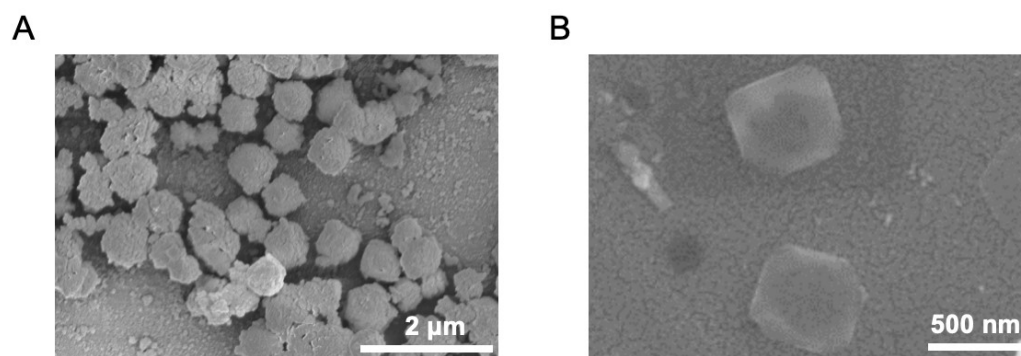
## 2. DFT calculations methods

We have employed the first-principles<sup>6,7</sup> to perform density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE)<sup>8</sup> formulation. We have chosen the projected augmented wave (PAW) potentials<sup>9, 10</sup> to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 500 eV. The DFT-D3 method incorporating the Becke-Johnson damping function was utilized for dispersion correction.<sup>11</sup> Partial occupancies of the Kohn-Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than  $10^{-6}$  eV. Ionic positions were optimized until the maximum force on any atom fell below 0.05 eV/Å in all Cartesian directions. The adsorption energy ( $E$ ) is defined as the difference between the total energy of the adsorption system and the sum of the energies of the isolated adsorbate and the clean substrate. It is calculated using the following formula:

$$E = E_{\text{tol}} - (E_{\text{sur}} + E_{\text{ads}})$$

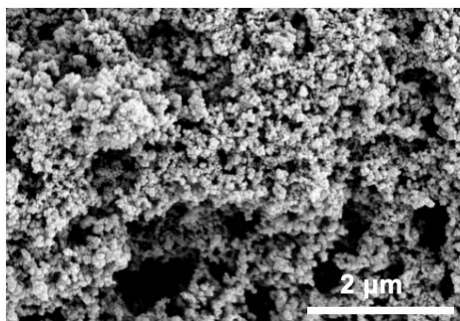
where  $E_{\text{tol}}$  represents the total energy of the fully optimized adsorbate-substrate system,  $E_{\text{sur}}$  denotes the energy of the clean substrate, and  $E_{\text{ads}}$  corresponds to the energy of the isolated adsorbate molecule. According to this definition, a negative value indicates an exothermic adsorption process, meaning the adsorbed system is thermodynamically stable.

### 3. Supplementary Figures and Tables

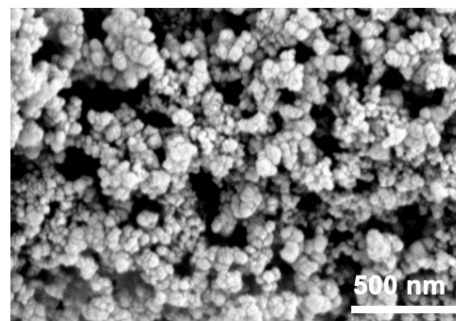


**Figure S1.** (A) and (B) SEM images of UiO-66-(COOH)<sub>2</sub>.

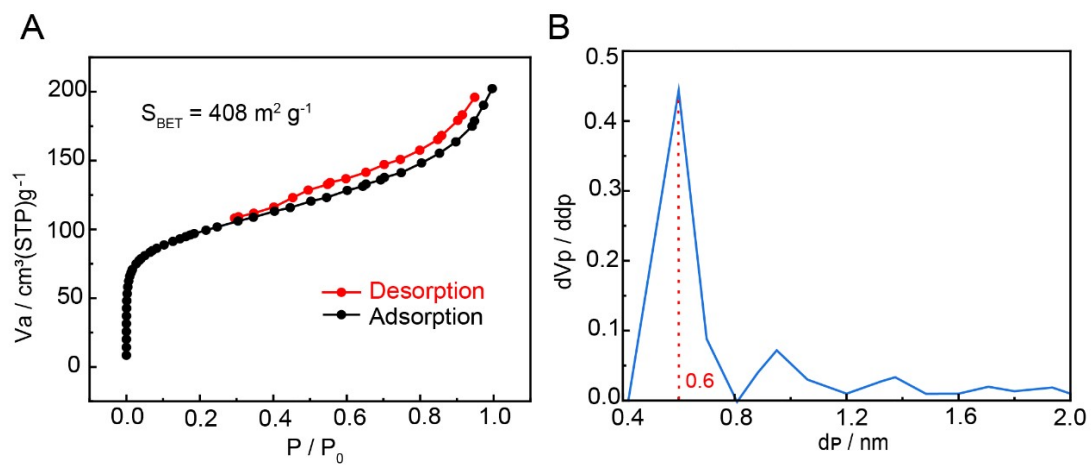
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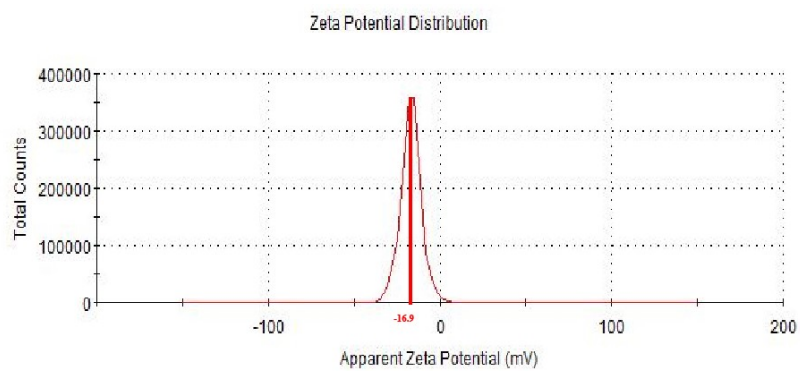
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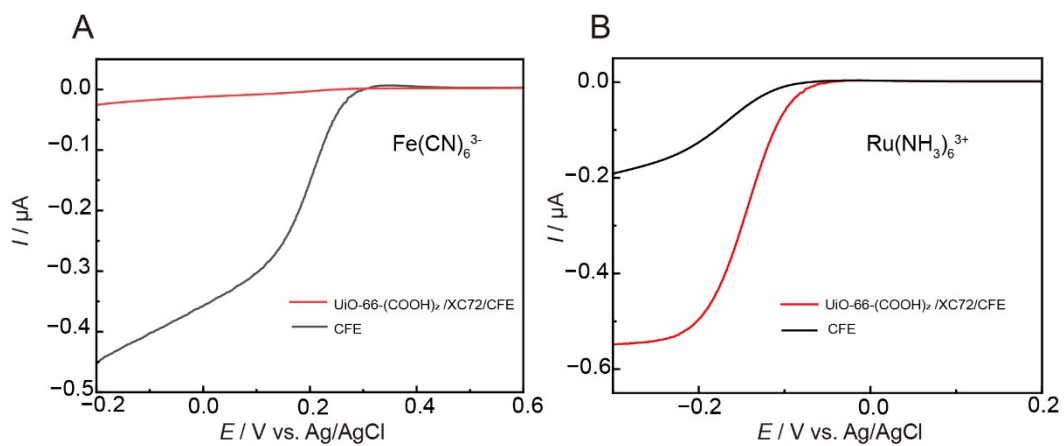
**Figure S2.** (A) and (B) SEM images of XC72.



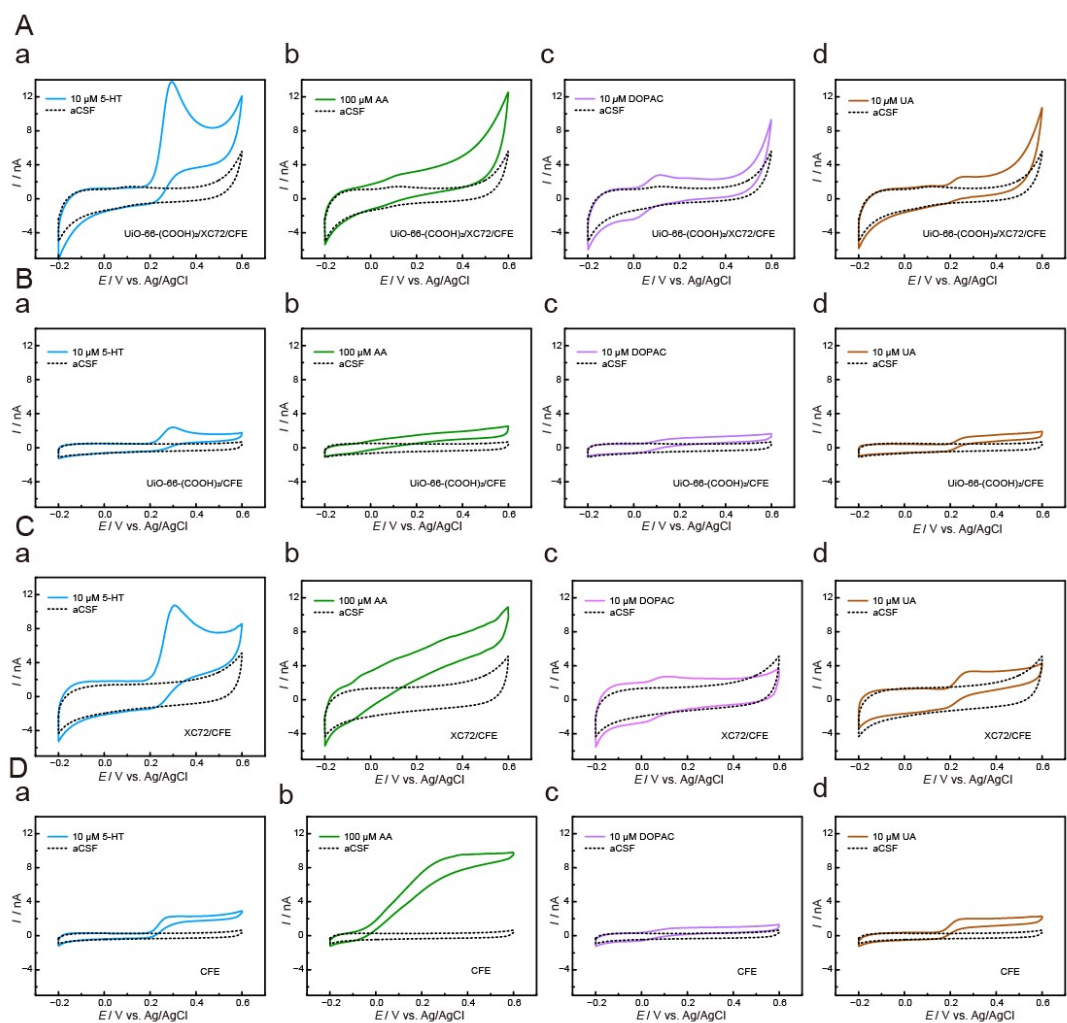
**Figure S3.** (A) Nitrogen sorption isotherms and calculated Brunauer–Emmett–Teller surface area ( $S_{\text{BET}}$ ). (B) pore size distributions of the UiO-66-(COOH)<sub>2</sub>.



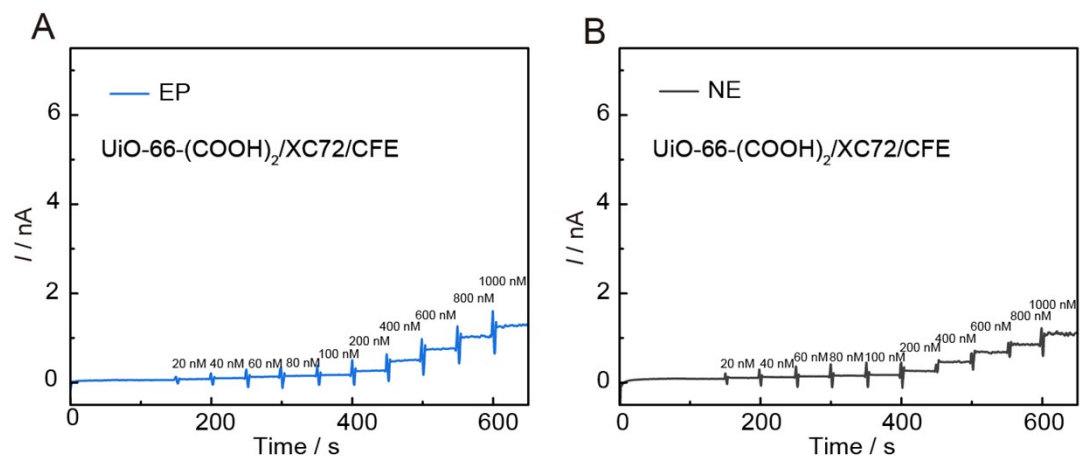
**Figure S4.** Zeta potential distribution of UiO-66-(COOH)<sub>2</sub>-H<sub>2</sub>O dispersion (1 mg/mL).



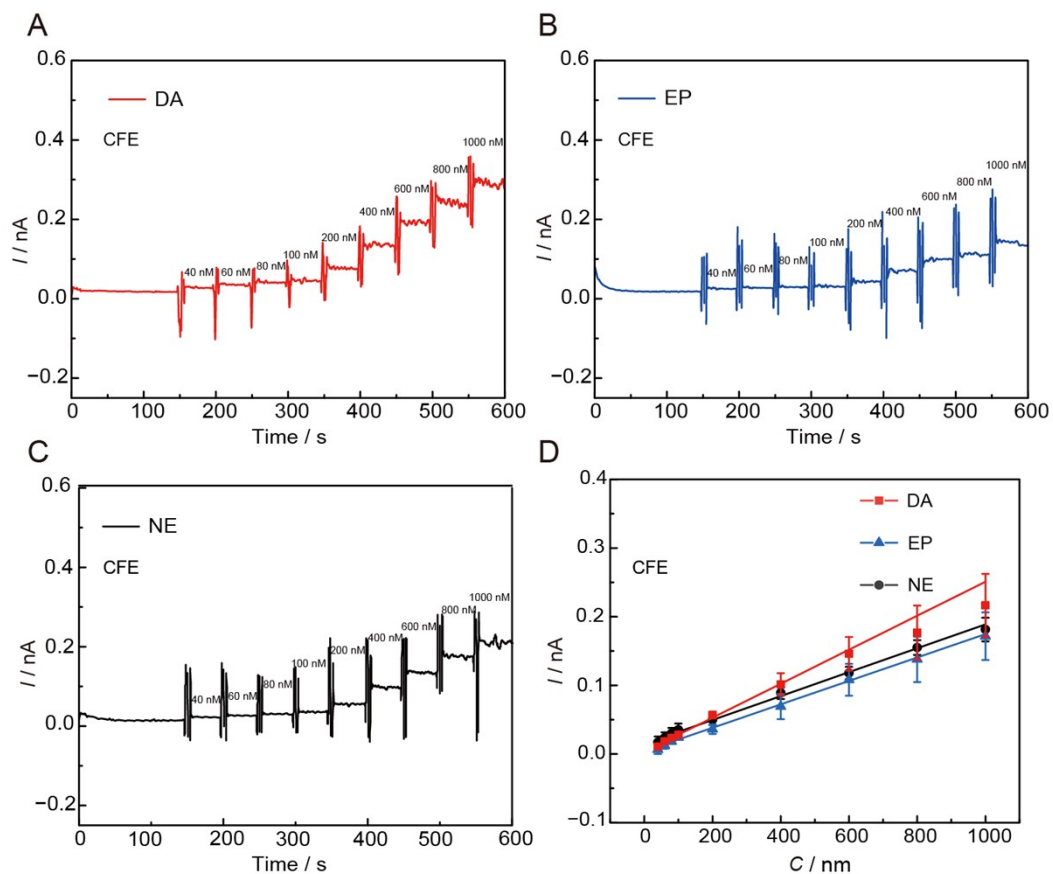
**Figure S5.** LSVs obtained with CFE (black) and UiO-66-(COOH)<sub>2</sub>/XC72/CFE (red) in 0.1 M KCl containing 5 mM  $\text{Fe}(\text{CN})_6^{3-}$  (A), 5 mM  $\text{Ru}(\text{NH}_3)_6^{3+}$  (B). The potential scan rate was 50 mV s<sup>-1</sup>.



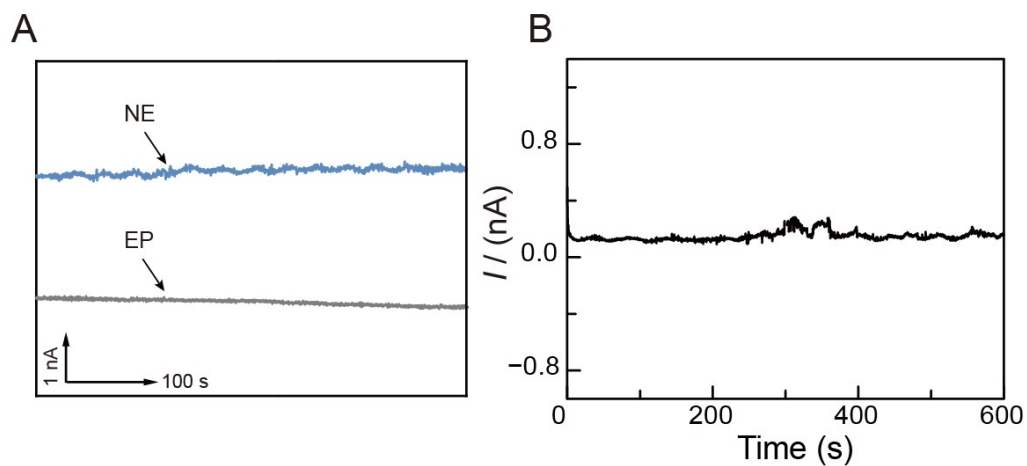
**Figure S6.** Typical CVs obtained at (A) UiO-66-(COOH)<sub>2</sub>/XC72/CFE, (B) UiO-66-(COOH)<sub>2</sub>/CFE, (C) XC72/CFE and (D) CFE in aCSF solution (pH 7.4) in the absence (dashed line) and presence (solid line) of (a) 10 μM 5-HT, (b) 100 μM AA, (c) 10 μM DOPAC and (d) 10 μM UA, respectively. The scan rate is 50 mV s<sup>-1</sup>.



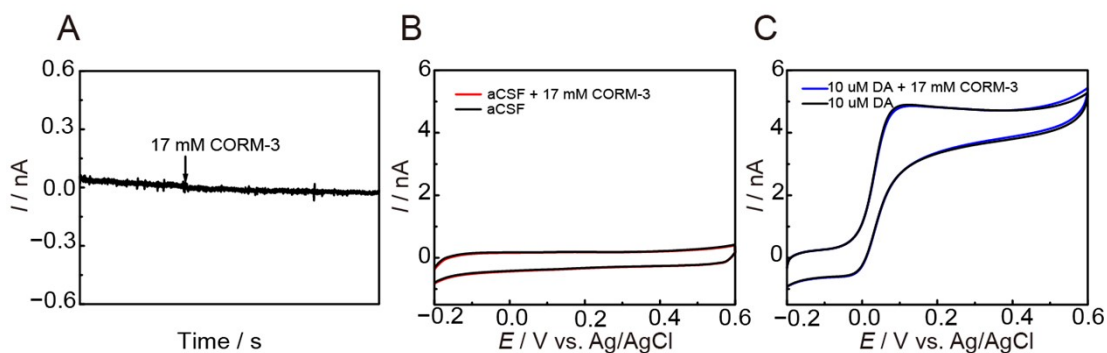
**Figure S7.** Amperometric response obtained with UiO-66-(COOH)<sub>2</sub>/XC72/CFE toward the successive addition of EP(A), NE(B) into aCSF solution. NE, EP concentrations: 20, 40, 60, 80, 100, 200, 400, 600, 800 and 1000 nM. Potential: +0.1 V (vs. Ag/AgCl).



**Figure S8.** Amperometric response obtained with CFE toward the successive addition of DA(A), EP(B), NE(C) into aCSF solution. DA, NE, EP concentrations: 40, 60, 80, 100, 200, 400, 600, 800 and 1000 nM. Potential: +0.1 V (vs. Ag/AgCl). (D) The current responses of CFE to DA, EP, NE in aCSF ( $n = 3$ , mean  $\pm$  SD).

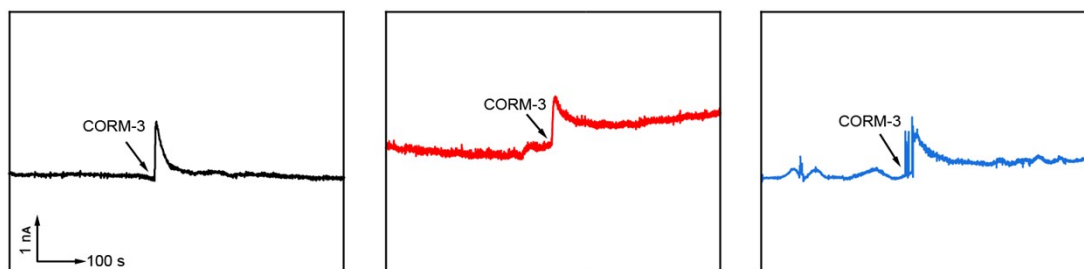


**Figure S9.** (A) Typical current response to local microinjection of 1  $\mu\text{M}$  NE or EP at a rate of 2  $\mu\text{L min}^{-1}$  for 30 s. (B) Typical amperometric response recorded in vivo with the UiO-66-(COOH)<sub>2</sub>/XC72/CFE for in vivo monitoring of extracellular DA in rat striatum. Potential: +0.1 V (vs. Ag/AgCl).



**Figure S10.** (A) Amperometric response obtained with UiO-66-(COOH)<sub>2</sub>/XC72/CFE toward the addition of 17 mM CORM-3 into aCSF solution. Potential: +0.1 V (vs. Ag/AgCl). (B) Voltammetric responses of UiO-66-(COOH)<sub>2</sub>/XC72/CFE in aCSF in the presence (red line) and absence (black line) of 17 mM CORM-3. (C) Voltammetric responses of UiO-66-(COOH)<sub>2</sub>/XC72/CFE to 10 μM DA in the presence (blue line) and absence (black line) of 17 mM CORM-3. Scan rate: 50 mV s<sup>-1</sup>.

Three stimuli in three rats , respectively



**Figure S11.** Amperometric responses recorded with the UiO-66-(COOH)<sub>2</sub>/XC72/CFE implanted in three rats' brains. Applied potential: +0.1 V (vs. Ag/AgCl).

**Table S1. The comparison of analytical performances between our sensor with other MOF-based DA sensors**

Electrodes	Method	LOD ( $\mu\text{M}$ )	Selectivity	In vivo applicability	Ref.
Ni-MOF/GCE	DPV	0.06	AA, UA	real sample	12
H-ZIF/GCE	Amperometry	0.012	Glu, Cys, AA, UA	urine sample	13
Zr-NDI/MWCNT/GCE	DPV	0.6	Glu, AA, UA	urine sample	14
UiO-66/Go/FTO	DPV	2.1	AA, UA	/	15
Cu-MOF/MWCNT-COOH/GCE	DPV	0.29	AA, CA, Glu, Leu	human serum sample	16
CoNi-MOF@ERGO/GCE	DPV	0.086	AA, Glu, Leu, Cys, Trp	human serum sample	17
Co-MOF-GO/1-M,3-BB/CPE	SWV	0.04	UA	urine sample	18
Apt/ZrNi-Fc/MXene/GCE	DPV	0.07	5-HT, L-Cys, Glu, urea, UA, AA	human serum sample	19
CuNZ-rGO/GCE	Amperometry	0.03	EP, NE, urea, UA, Glu, Cys, GSH, AA	living cells	20
Au/RP1/Ni <sub>3</sub> HHTP <sub>2</sub> /CFE	DPV	0.001	AA, UA, NE, EP, DOPAC, 5-HT, 3-MT, 5-HIAA, HVA, ATP, Glu, Lac	in PD Mouse Brains	21
UiO-66-(COOH) <sub>2</sub> /XC72/CFE	Amperometry	0.00167	NE, EP, AA, UA, DOPAC, 5-HT	in vivo rat brain	this work

AA = Ascorbic acid; UA = Uric acid; DOPAC = 3,4-Dihydroxyphenylacetic acid; 5-HT = 5-Hydroxytryptamine; NE = Norepinephrine; EP = Epinephrine; Glu = Glucose; Cys = Cysteine; GSH = Glutathione; Trp = Tryptophan; Leu = Leucine; CA = Citric acid; 3-MT = 3-Methoxytyramine; 5-HIAA = 5-Hydroxyindole-3-acetic acid; HVA = Homovanillic Acid; ATP = Adenosine Triphosphate; Lac = Lactic Acid; DPV = Differential Pulse Voltammetry; SWV = Square Wave Voltammetry.

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