# **Supplementary Information**

# An electrolyte-gated polythiophene transistor for the detection of biogenic amines in water

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#### 1. General

Reagents and solvents used for this research were commercially available and used as supplied. A glass substrate (model: Eagle XG) was purchased from Corning, Inc. Cytop (model: CTX-809SP2) and perfluorotributylamine (CAS: 311-89-7) were kindly supplied from Asahi Glass Co. Ltd. Cytop used for deposition of a hydrophobic thin-film was diluted using perfluorotributylamine. Poly{3-(5-carboxypentyl)thiophene-2,5-diyl} (P3CPT) was purchased from Rieke Metals, Inc. Gold for vacuum deposition was purchased from Tanaka Kikinzoku Kogyo Co., Ltd. Dimethyl sulfoxide (DMSO) (CAS: 67-68-5), sulfuric acid (CAS: 7664-93-9), hydrochloric acid (CAS: 7647-01-0), sodium hydroxide (CAS: 1310-73-2), trimethylamine hydrochloride (CAS: 593-81-7), and sodium chloride (CAS: 7647-14-5) were purchased from Kanto Chemicals. Hydrogen peroxide (CAS: 7722-84-1) was purchased from Wako Pure Chemical Industries, Ltd. Histamine dihydrochloride (CAS: 56-92-8) and tyramine hydrochloride (CAS: 60-19-5) were purchased from Sigma-Aldrich Co. LLC. L-Histidine (CAS: 71-00-1), methylamine hydrochloride (CAS: 593-51-1), dimethylamine hydrochloride (CAS: 506-59-2), Lmethionine (CAS: 63-68-3), L-cystine (CAS: 56-89-3), ornithine dihydrochloride (CAS: 6211-16-1), L-(+)-lysine (CAS: 56-87-1), glycine (CAS: 56-40-6), L-alanine (CAS: 56-41-7), L-phenylalanine (CAS: 63-91-2), and putrescine (CAS: 110-60-1) were purchased from Tokyo Kasei Co. Ltd. 2-Morpholinoethanesulfonic acid monohydrate (MES) (CAS:

145224-94-8) was purchased from Dojindo Laboratories. The electrolyte solutions were prepared using Milli-Q water (18 M $\Omega$  cm at 25 °C).

The UV-vis spectra were measured using a double beam UV-vis spectrophotometer (model: UV-2600) from Shimadzu Corporation. UV-vis spectra were recorded from 300 nm to 800 nm. Metal electrodes were deposited by using a vacuum evaporator equipment (model: SVC-700TMSGS) from Sanyu Electron Co., Ltd. An oxygen reactive ion etching (O<sub>2</sub>-RIE) was performed on a dry etching system (model: RIE-10NG) from SAMCO, Inc. The thin-film deposition was performed on a spin coater equipment (model: 1H-D7) from MIKASA Co., Ltd. The baking or annealing treatment of the substrate was performed on a digital hot plate apparatus (model: HP-2SA) from AS ONE Corp. The pH values of solution were measured by a pH meter (model: D-51) from Horiba, Ltd. The electrical characteristics of the polymer TFT devices were measured using source meter equipment (model: 2636B or 2602B) from Keithley Instruments. The thin-film topographic image and the cross-section profile of polymers were obtained using an atomic force microscope (AFM) (model: VN-8010) from KEYENCE Corp. The infrared (IR) spectra were measured using a Fourier transform infrared spectrophotometer (FT-IR) (model: Nicolet iS5) from Thermo Fisher Scientific Inc.

#### 2. Fabrication of the electrolyte-gated TFT utilizing P3CPT

The polymer TFT devices were fabricated on the glass substrate (Eagle XG) which was cleaned by a piranha solution ( $H_2O_2 / H_2SO_4 = 1 / 4$ , v/v). Gold (Au) was used as source, drain, and gate electrodes (50 nm in thickness) and deposited on the glass substrate by resistance heating evaporation at a rate of 0.1–0.5 Å s<sup>-1</sup> under pressure of 10<sup>-4</sup> Pa (Fig. S1, step 2). The elctrodes were patterned using a stainless steel shadow-mask. The channel width and length for the resulting polymer TFT device were 1000 and 50 µm, respectively. perfluoropolymer amorphous (Cytop) (4.5)wt%) solution of An in a perfluorotributylamine was spin-coated at the rotational speed of 500 rpm for 5s, and then 4000 rpm for 60s (150 nm in thickness) (Fig. S1, step 3). The Cytop-coated substrate was baked on the hot plate at 150 °C for 30 min. To prepare the hydrophobic banks at the channel and the gate regions, the Cytop thin-film was patterned by oxygen plasma etching with a shadow-mask (Fig. S1, step 4). The plasma power was 150 W and the treatment duration was 1.5 min. Subsequently, a semiconducting polymer, P3CPT was drop-casted from a 0.05 wt% solution of dimethyl sulfoxide (DMSO), and then annealed at 110 °C for 12 h in a nitrogen-filled glove box ([O<sub>2</sub>]: < 1 ppm, [H<sub>2</sub>O]: < 1 ppm) (Fig. S1, step 5). Finally, an electrolyte solution was dropped onto the fabricated device (Fig. S1, step 6).

The droplet volume of the electrolyte solution was 50  $\mu$ L. The thickness of each film was determined by a tapping mode measurement of AFM.



Fig. S1 Schematic illustration of the fabrication process.



Fig. S2 Surface topography of the thin-film of P3CPT.



**Fig. S3** (a) Surface topography of edge of the hydrophobic bank at the channel region. (b) The cross-section profile at the same region.

#### **3.** The determination of the p*K*<sub>a</sub> value of P3CPT<sup>1</sup>

pH-Dependent transfer characteristics of the polymer TFT using P3CPT were obtained. The drain current at  $V_{DS}=V_{GS}=-0.3V$  decreased at above pH 3. The p $K_a$  value could be calculated from the data (Fig. 3) using the following equation:  $I = (I_0 + I_{max}K_a[H^+])/(1 + K_a[H^+])$  when I is the drain current for a particular concentration of proton;  $I_0$  is initial current of the titration experiment;  $I_{max}$  is the maximum current in the titration experiment;  $K_a$  is the acid dissociation constant; [H<sup>+</sup>] is the concentration of proton. The  $pK_a$  profile can be analyzed using nonlinear curve fitting based on the Levenberg-Marquardt algorithm in Origin (Originlab Corp.), and calculated to be 4.2.

#### 4. Titrations

To compare the changes of the device characteristics upon the addition of each analyte (Fig. 5), the obtained current was normalized as  $(I-I_0) / I_0$ . *I* and  $I_0$  denote the observed drain current of the polymer TFT upon the addition of an analyte and the drain current in the absence of an analyte, respectively. The drain current measured at  $V_{GS} = V_{DS} = -0.3$  V.



**Fig. S4** Transfer characteristics ( $I_{DS}$ - $V_{GS}$ ) of the polymer TFT upon addition of increased amounts of putrescine in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5. at r.t. [Putrescine] = 0 – 10 mM.



**Fig. S5** (b) The gate-source current of the polymer TFT upon titration with putrescine in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at r.t. [Putrescine] = 0 - 10 mM.



**Fig. S6** Transfer characteristics ( $I_{DS}$ - $V_{GS}$ ) of the polymer TFT upon addition of increased amounts of tyramine in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5. at r.t. [Tyramine] = 0 - 10 mM.



**Fig. S7** The gate-source current of the polymer TFT upon titration with tyramine in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at r.t. [Tyramine] = 0 - 10 mM.



**Fig. S8** Transfer characteristics ( $I_{DS}$ - $V_{GS}$ ) of the polymer TFT upon addition of increased amounts of histidine in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5. at r.t. [Histidine] = 0 - 10 mM.



**Fig. S9** The gate-source current of the polymer TFT upon titration with histidine in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at r.t.



**Fig. S10** The gate-source current of the polymer TFT upon titration with histamine in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at r.t. [Histamine] = 0 - 10 mM.

#### 5. Reusability



Fig. S11 Changes in the output current upon alternatively dropping a MES buffer solution with or without histamine onto the device. The relative standard deviation of each response is  $\leq 6\%$ .



6. Selectivity

**Fig. S12** Drain current changes in the electrolyte-gated TFT after addition of various analytes to a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at r.t. [Analyte] = 8 mM. (a) methylamine, (b) dimethylamine, (c) trimethylamine, (d) tyramine, (e) putrescine, (f) methionine, (g) histamine, (h) histidine, (i) cystine, (j) ornithine, (k) lysine, (l) glycine, (m) alanine, (n) phenylalanine. The relative standard deviation of each response is  $\leq 8\%$ .

## 7. UV-vis measurement for P3CPT



Fig. S13 UV-vis spectra of P3CPT upon the addition of histamine in DMSO at r.t. [Histamine] =  $0 - 15 \mu$ M. The data were collected within 3 min after mixing P3CPT with histamine.

# 8. FT-IR measurement for P3CPT



Fig. S14 FT-IR spectra (KBr pellet) of P3CPT in the (a) absence or (b) presence of histamine.

#### 9. Reference

1 Y. Kubo, T. Ishida, T. Minami and T. D. James, Chem. Lett., 2006, 35, 996.