

Electrical Supplementary Information

Detection of polyamines by an extended gate-type organic transistor functionalized with a carboxylate attached 1,3,4-thiadiazole derivative

Koichiro Asano,^a Yui Sasaki,^a Qi Zhou,^a Riho Mitobe,^a Wei Tang,^a Xiaojun Lyu,^a Masao Kamiko,^a Hikaru Tanaka,^b Akari Yamagami,^b Kazutake Hagiya,^b and Tsuyoshi Minami^{a*}

^a Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo, 153-8505, Japan.

E-mail: tminami@iis.u-tokyo.ac.jp

^b Corporate Research Center, Toyobo Co., Ltd., 2-1-1 Katata, Otsu, Shiga, 520-0292, Japan.

Contents

1. Fabrication of the extended-gate-type OTFT	S2
2. Characterization of the extended-gate electrode	S3
3. Electrochemical measurements	S4
4. Basic characteristics of the OTFT	S5
5. Selected electrical titrations of polyamines	S6
6. Reusability test	S7
7. XPS results	S8
8. Linear discriminant analysis	S8
9. Quantitative analysis	S9
10. Reference	S10

1. Fabrication of the extended-gate-type OTFT

An Al gate electrode (30 nm in thickness) was fabricated using the vacuum thermal evaporation (SVC-700TMSG/SVC-7PS80, SANYU Electron) on a glass substrate with a metal mask. The glass substrate was washed by a piranha solution ($\text{H}_2\text{O}_2 : \text{H}_2\text{SO}_4 = 1 : 4$) before the Al deposition. Reactive ion etching (SAMCO RIE-10NR) was applied to form an AlO_x dielectric layer by oxygen plasma treatment. Next, the treated substrate was immersed in 2-propanol containing tetradecylphosphonic acid (TDPA, 10 mM) for 16 h at 25 °C to fabricate an AlO_x /TDPA dielectric layer. Subsequently, the vacuum thermal evaporation method was employed to deposit Au electrodes as source and drain (30 nm in thickness) on the dielectric layer with the metal mask. The channel width and length of the device were 1000 and 50 μm , respectively. As an organic semiconductor (OSC) layer, 1,2-dichlorobenzene containing poly{2,5-bis(3-hexadecylthiophene-2-yl)thieno[3,2-*b*]thiophene} (PBTTT) (0.03 wt%) was drop-casted onto the channel area, and the substrate was baked at 160 °C for 10 min. Finally, Cytop[®] (CTL-809M in CT-Solv.180, ratio 1 : 1 (v/v)) was spin-coated on the OSC layer and baked at 110 °C for 10 min to form the passivation layer.¹

2. Characterization of the extended-gate electrode

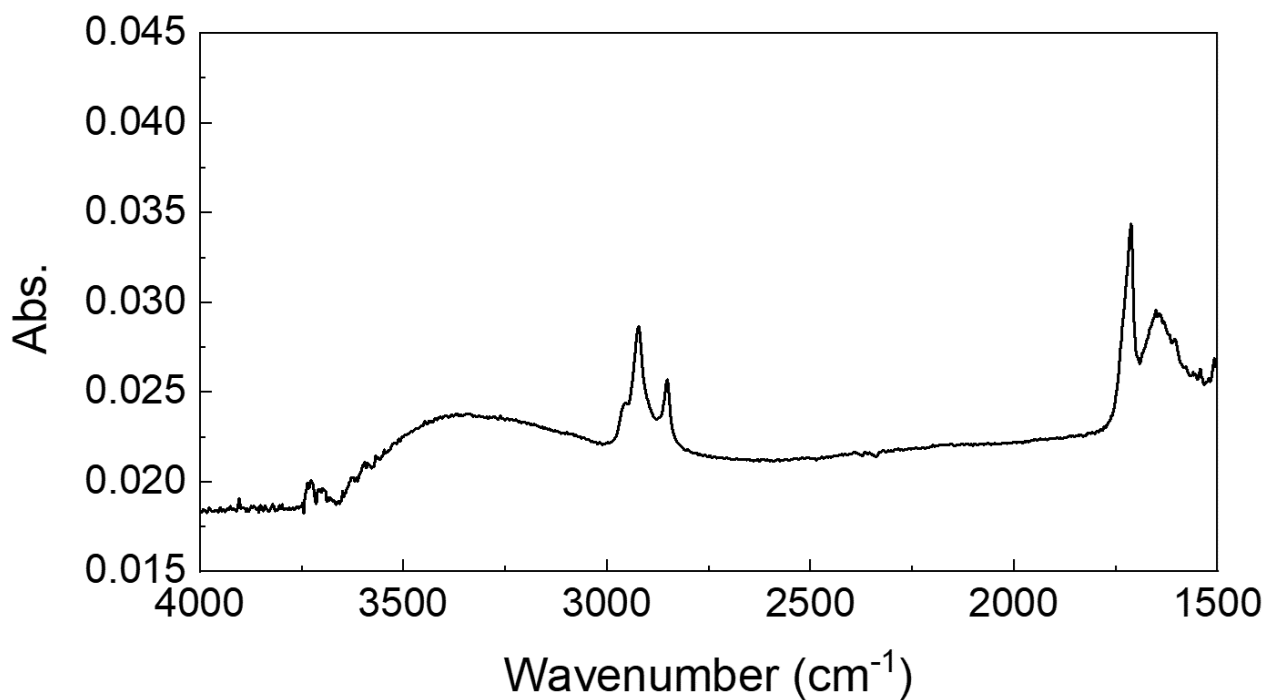


Fig. S1 FT-IR (ATR) spectra of the TMT-Au electrode.

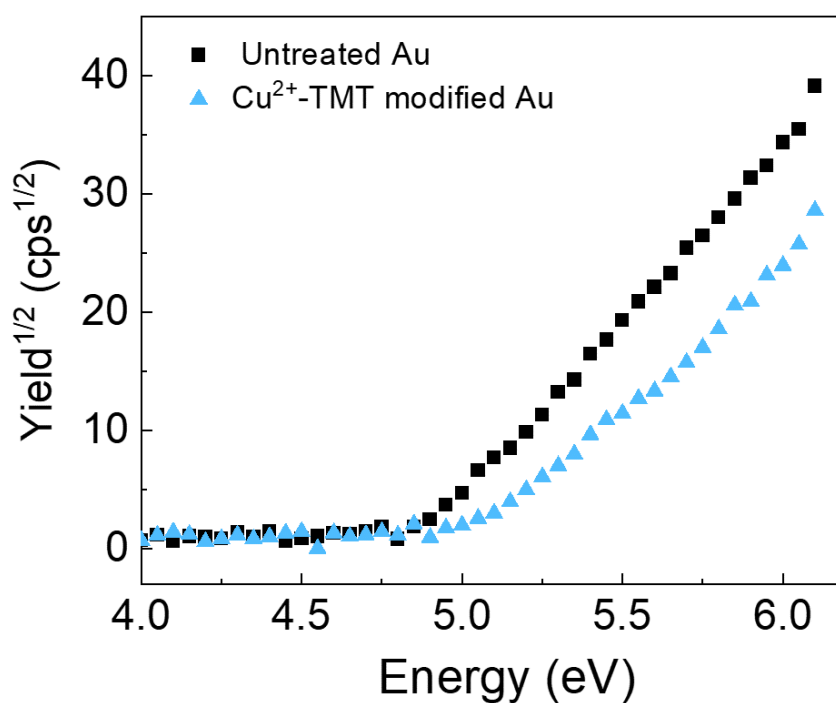


Fig. S2 PYS results of the untreated Au (black square) and the Cu²⁺-TMT modified Au (pastel blue triangle) electrodes in air.

3. Electrochemical measurements

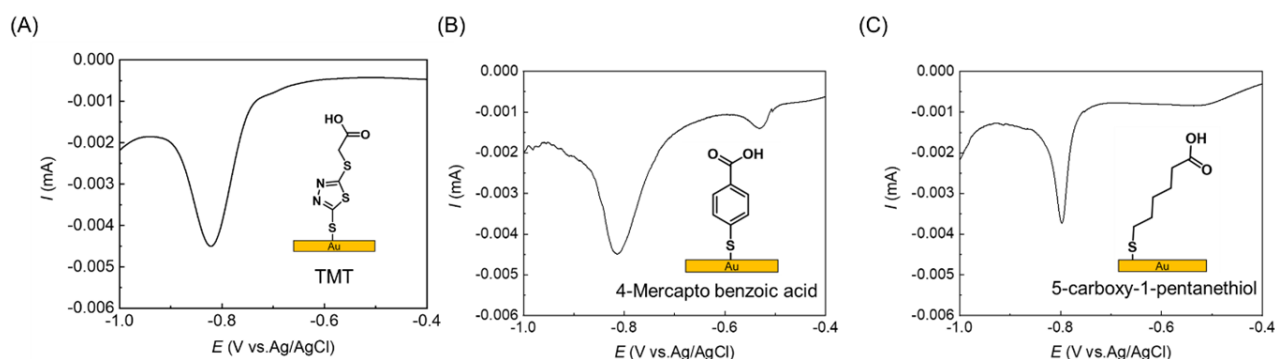


Fig. S3 Linear sweep voltammetry of the molecular density test in the KOH solution (0.1 M). Potential scans from 0 V to -1.6 V, and the scan rate was set to be 20 mV/s. Molecular densities were calculated according to Faraday's law with the integration of the peak areas: (A) TMT, 9.65×10^{-10} mol/cm², (B) 4-mercapto benzoic acid, 9.60×10^{-10} mol/cm², and (C) 5-carboxy-1-pentanethiol, 6.65×10^{-10} mol/cm².

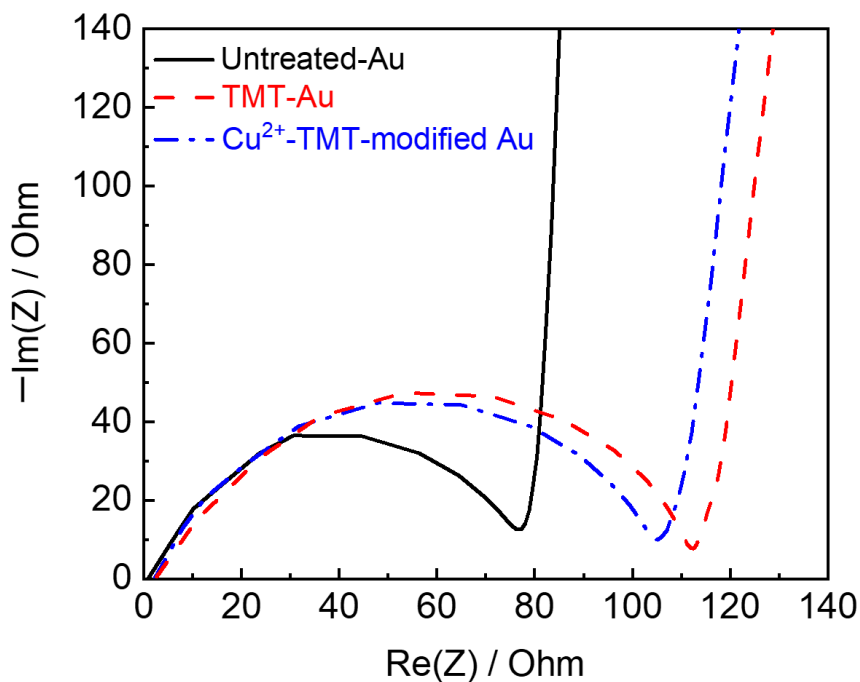


Fig. S4 Electrochemical impedance spectroscopy of the untreated-Au (black solid line), the TMT-Au (red dash line), and the Cu²⁺-TMT-modified-Au (blue dash-dot line) electrodes. The charge-transfer resistance was estimated from the diameter of the semicircle.

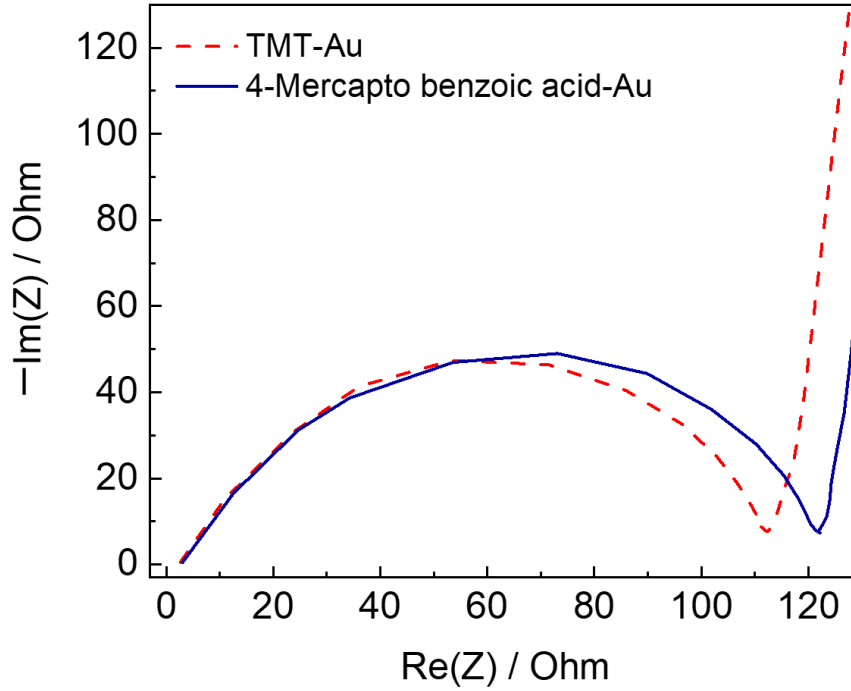


Fig. S5 Electrochemical impedance spectroscopy of the TMT-Au (red dash line) and the 4-mercapto benzoic acid-Au (blue line) electrodes. The charge-transfer resistance was estimated from the diameter of the semicircle.

4. Basic characteristics of the OTFT

The electrical characteristics of the fabricated OTFT device were evaluated using source meters. The gate voltage (V_{GS}) was applied through the combination of the extended-gate and Ag/AgCl reference electrodes immersed in a CHES buffer (50 mM, pH 8.5 at 25 °C). For transfer characteristics ($V_{GS}-I_{DS}$), a constant drain voltage ($V_{DS} = -1$ V) was applied to the drain electrode, and the sweep voltage (V_{GS}) was applied to the gate electrode from 0.5 V to -3 V. The measurement was repeated for three times. For output characteristics ($V_{DS}-I_{DS}$), V_{DS} was swept from 0 V to -3 V, while V_{GS} was set from 0 V to -3 V at -1 V steps.

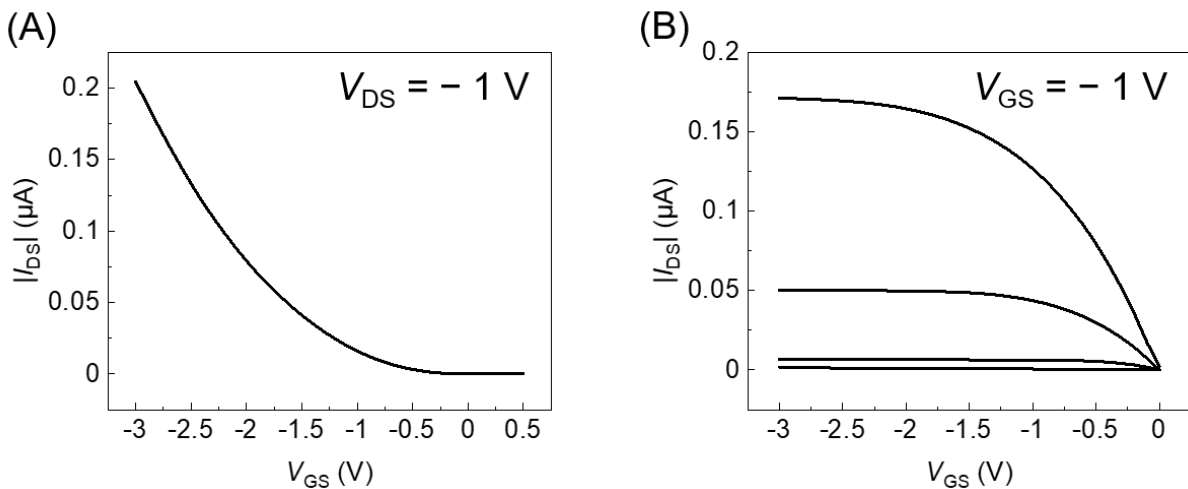


Fig. S6 (a) Transfer and (b) output characteristics of the fabricated OTFT.

5. Selected electrical titrations of polyamines

For the detection of polyamines, a CHES buffer solution (50 mM, pH 8.5) with NaCl (10 mM) was prepared. After mixing target amines (0–150 μM) with the buffer in the presence of the reference and extended-gate electrodes, the solution was left for 10 min before the measurements. At each concentration, the measurements were tested for three times and the data was used for further analysis such as pattern recognition.

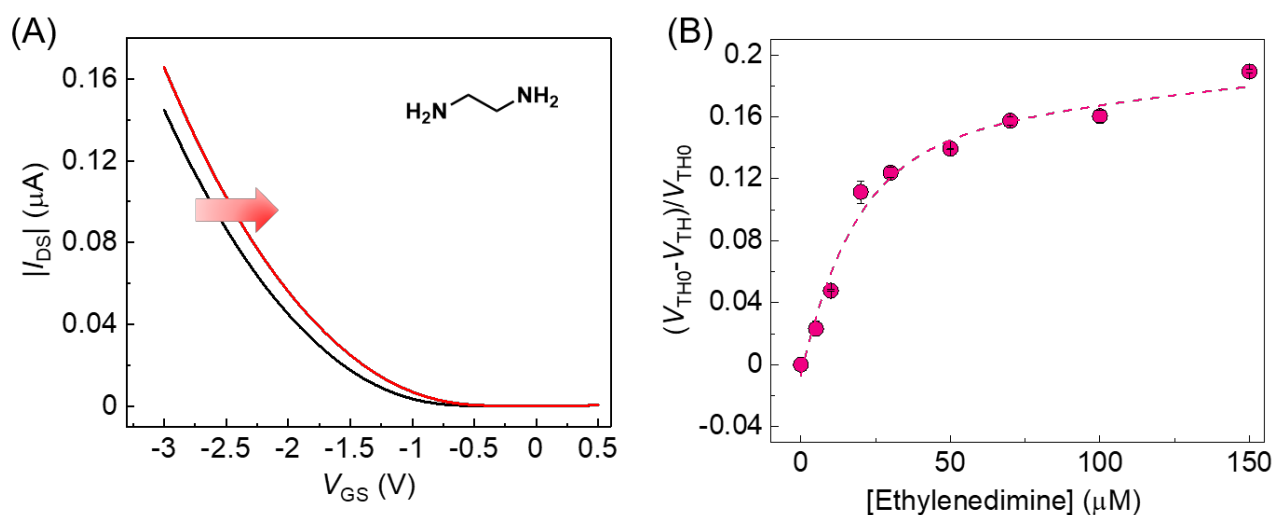


Fig. S7 (A) Changes in transfer characteristics ($V_{\text{GS}}-I_{\text{DS}}$) and (B) titration isotherm of the OTFT-based sensor upon the addition of ethylenediamine in a 50 mM CHES buffer solution with 10 mM NaCl at pH 8.5 at 25 $^{\circ}\text{C}$. [Ethylenediamine] = 0–150 μM .

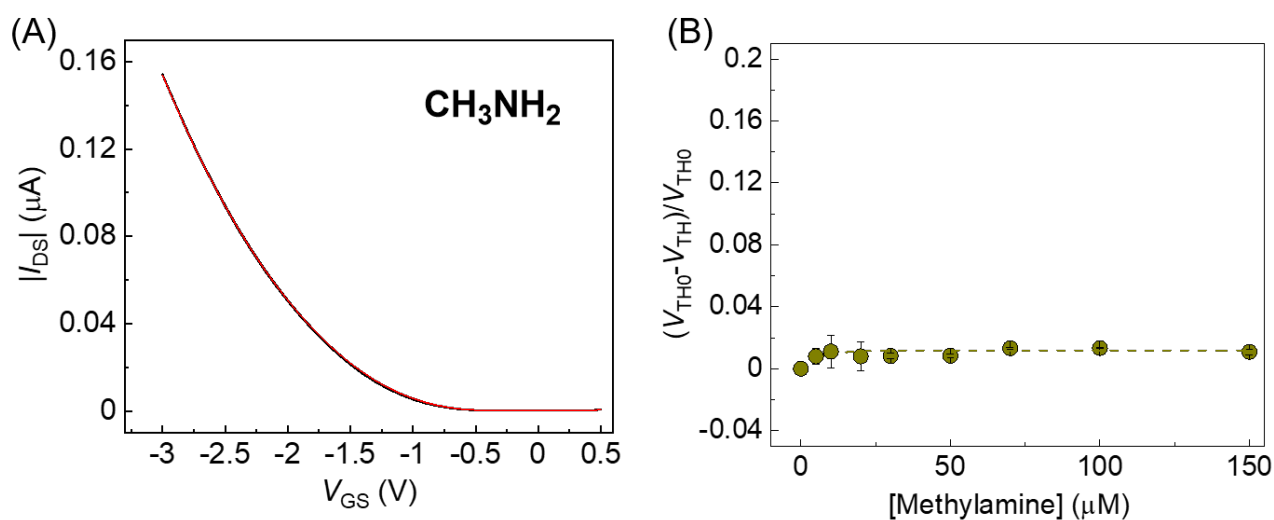


Fig. S8 (A) Changes in transfer characteristics ($V_{\text{GS}}-I_{\text{DS}}$) and (B) titration isotherm of the OTFT-based sensor upon the addition of methylamine in a 50 mM CHES buffer solution with 10 mM NaCl at pH 8.5 at 25 $^{\circ}\text{C}$. [Methylamine] = 0–150 μM .

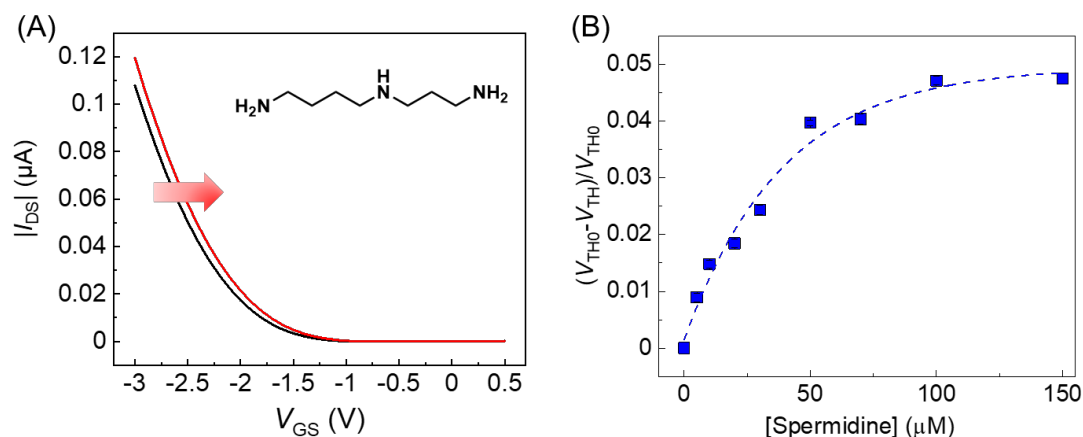


Fig. S9 (A) Changes in transfer characteristics (V_{GS} - I_{DS}) and (B) titration isotherm of the OTFT-based sensor upon the addition of spermidine in a 50 mM CHES buffer solution with 10 mM NaCl at pH 8.5 at 25 °C. [Spermidine] = 0–150 μ M.

6. Reusability test

We evaluated the reusability of the OTFT-based sensor. The V_{TH} change upon adding spermine could be recovered after immersing into an aqueous solution containing $\text{Cu}(\text{ClO}_4)_2$ and rinsing with DI water. We then re-immersed the electrode in the aqueous solution with spermine, and the positive shift of V_{TH} was observed. This cycle process was operated for 5 times, and the reversible response of the OTFT was obtained as expected. Although the gradual decrease of the response to spermine, which might be derived from residual spermine on the electrode in the repeated use, should be improved, we showed the potential of the reusability of the Cu^{2+} -TMT complex-based SAM OTFT. Several amines such as putrescine would remain on the Au surface, implying that it is hard to reuse the electrode. Nonetheless, the extended gate electrode is separated from the OTFT part, meaning that we can easily change the electrode. Thus, we can select either the washing process, which is to reuse the electrode with amines that cause positive V_{TH} shifts, or the exchanging process for amines with negative V_{TH} shifts.

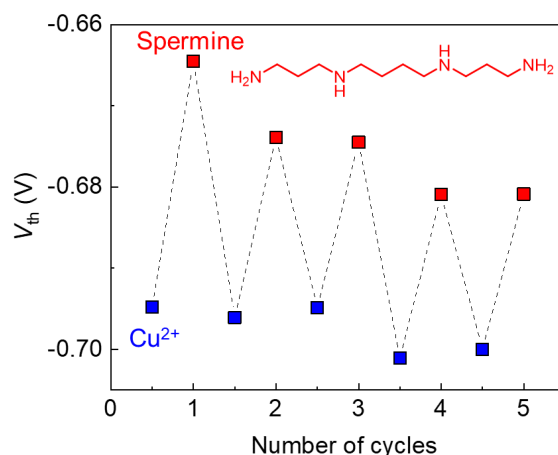


Fig. S10 The reusability for the OTFT-based sensor. After each spermine detection, the electrode was immersed in a HEPES buffer solution (100 mM, pH 7.4 at 25 °C) containing Cu^{2+} (1 mM), and washed with DI water, and then spermine was added repeatedly. The detection of spermine was carried out in a CHES buffer solution (50 mM, pH 8.5 at 25 °C) containing 10 mM NaCl.

7. XPS results

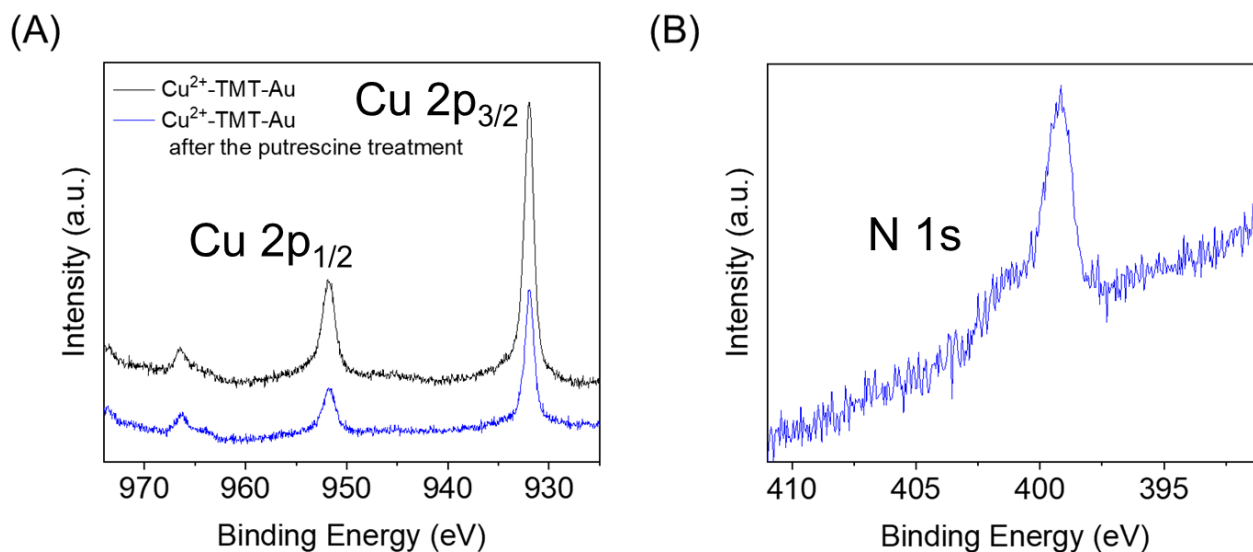


Fig. S11 XPS results of the Cu²⁺-TMT-electrode (black line) and the Cu²⁺-TMT-electrode after the putrescine treatment (blue line). The peaks were assigned to (A) Cu 2p and (b) N 1s.

8. Linear discriminant analysis

The discrimination of nine polyamines were carried out using linear discriminant analysis (LDA). The calculation software SYSTAT13 was purchased from HULINKS.

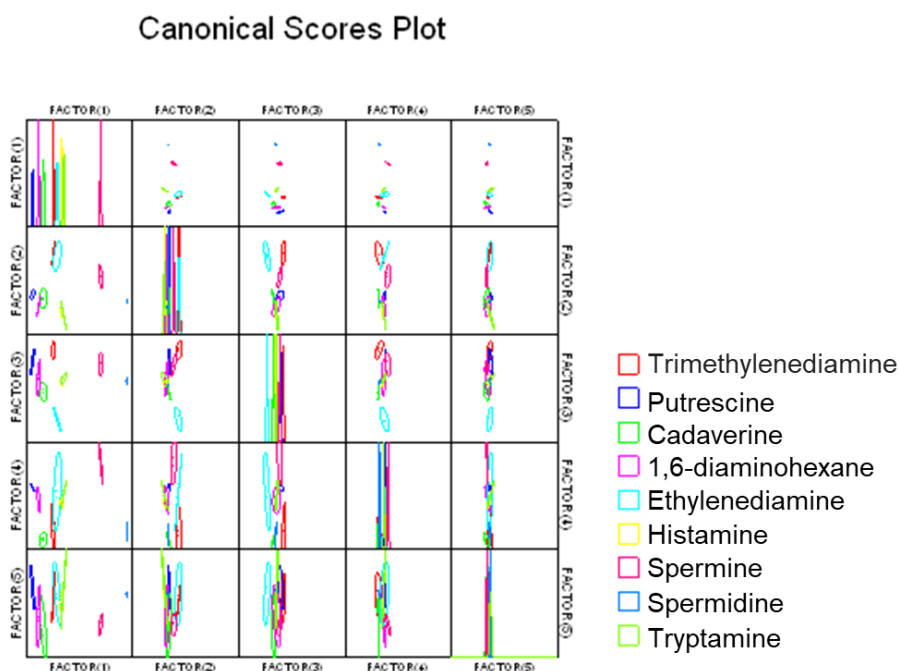


Fig. S12 Canonical score plots for polyamine discrimination.

Table S1 The jackknifed classification matrix of polyamine discrimination

Jackknifed Classification Matrix

	1,3-diaminopropane	1,4-diaminobutane	1,5-diaminopentane	1,6-diaminohexane	Ethylenediamine	Histamine	Sperimine
1,3-diaminopropane	3	0	0	0	0	0	0
1,4-diaminobutane	0	3	0	0	0	0	0
1,5-diaminopentane	0	0	3	0	0	0	0
1,6-diaminohexane	0	0	0	3	0	0	0
Ethylenediamine	0	0	0	0	3	0	0
Histamine	0	0	0	0	0	3	0
Sperimine	0	0	0	0	0	0	3
Spermidine	0	0	0	0	0	0	0
Tryptamine	0	0	0	0	0	0	0
Total	3	3	3	3	3	3	3

Jackknifed Classification Matrix (Contd.)

	Spermidine	Tryptamine	%correct
1,3-diaminopropane	0	0	100
1,4-diaminobutane	0	0	100
1,5-diaminopentane	0	0	100
1,6-diaminohexane	0	0	100
Ethylenediamine	0	0	100
Histamine	0	0	100
Sperimine	0	0	100
Spermidine	3	0	100
Tryptamine	0	3	100
Total	3	3	100

9. Quantitative analysis

For the real sample test, a commercially available fresh juice (Sembikiya-Sohonten, Ltd., Alphonso Mango Juice) was used to perform quantitative analysis of spermine based on the Cu²⁺-TMT-functionalized OTFT device. The juice sample was first centrifuged at 12000 rpm for 10 min to remove the unsolvable matters. Then, the supernatant solution was added into a CHES buffer solution (50 mM, pH 8.5) containing 10 mM NaCl and applied to chemical sensing using the OTFT without further pretreatments. The solution was left for 10 min before the electrical measurements, and the evaluation was carried out with three repetitions for each concentration of spermine (0–120 μM).

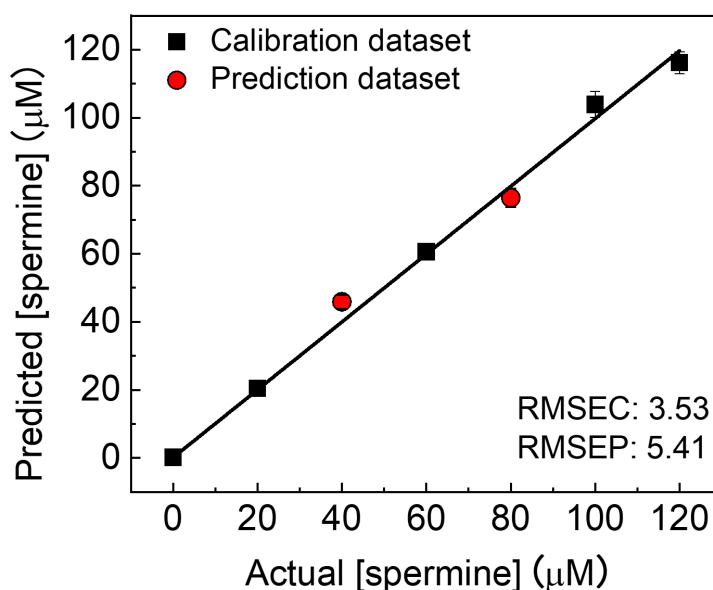


Fig. S13 SVM regression analysis for spermine in the diluted mango juice. The root-mean-square errors of calibration and prediction confirmed the accuracy of the established model.

10. Reference

1. T. Minamiki, T. Minami, R. Kurita, O. Niwa, S.-i. Wakida, K. Fukuda, D. Kumaki and S. Tokito, *Appl. Phys. Lett.*, 2014, **104**, 243703.