

Electronic Supplementary Information

An extended-gate-type organic transistor for monitoring the Menschutkin reaction of tetrazole at a solid–liquid interface

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1. General

Reagents and materials

Commercially available reagents and supplied materials were used for the OFET fabrication and chemical sensing without pre-treatments.

For fabrication of the OFET device: An OFET device was fabricated on a glass substrate (model: Eagle XG, 2 cm × 2.5 cm, Corning, Inc.). Metal electrodes were fabricated using an aluminum (Al) wire (1ϕ) (Furuuchi Chemical Co., Ltd.) and a gold (Au) particle (Tanaka Kikinzoku Kogyo Co., Ltd.). Tetradecylphosphonic acid (TDPA, Tokyo Chemical Industry Co., Ltd.) was employed to form a dielectric layer. Poly{2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene} (PBTTC-14) and 1,2-dichlorobenzene were obtained from Merck KGaA. 2-Propanol was purchased from Kanto Chemical Co. Inc. An amorphous hydrophobic material (CYTOP™, model: CTL-809M) was supplied from AGC Co., Ltd.

For fabrication of the extended-gate-electrode: Tris(2-carboxyethyl)phosphine (TCEP) hydrochloride as a reducing agent and methanol were obtained from FUJIFILM Wako Pure Chemical Industries, Ltd. and Kanto Chemical Co. Inc., respectively. A polyethylene naphthalate (PEN) film and 1-hydroxyethyl-5-mercapto-1*H*-tetrazole (EMT) were supplied from TOYOBO Co., Ltd.

For electrical measurements: An Ag/AgCl electrode as a reference electrode (RE-1B) and a Pt wire as a counter electrode were purchased from BAS Inc. A conductive silver paste (model: D-500), potassium chloride (KCl), sodium chloride (NaCl), and iodomethane (CH₃I) were obtained from FUJIFILM Wako Pure Chemical Industries, Ltd. Electrophiles obtained from Tokyo Chemical Industry Co., Ltd. were iodoethane (CH₃CH₂I), 2-iodopropane ((CH₃)₂CH-I), 2-iodo-2-methylpropane ((CH₃)₃C-I), bromoethane (C₂H₅Br), and methyl trifluoromethanesulfonate (CF₃SO₃CH₃). 4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) was purchased from Dojindo Laboratories Co., Ltd. All aqueous solutions were prepared by using Milli-Q water (18.2 MΩ·cm).

For ¹H NMR analysis: Methanol-*d*₄ was obtained from Cambridge Isotope Laboratories, Inc. Methanol was used as internal reference.

Apparatuses

Techniques	Apparatus
Vacuum thermal deposition	SVC-700TMSGs, Sanyu Electron Co., Ltd.
Reactive ion etching (RIE)	SAMCO RIE-10NR
UV/O ₃ treatment	ASM4010Z, ASUMI GIKEN Co., Ltd.
Spin coat	MIKASA SPINCOATER 1H-D7
Measurements of the OFET characteristics	2612B, Keithley
Linear sweep voltammetry (LSV)	SP-300 potentiostat, Biologic
Photoelectron yield spectroscopy (PYS) in air	AC-2, Riken Keiki, Co.
Contact angle measurements	CA-X contact Angle goniometer, Kyowa interface science Co., Ltd.
pH Adjustment	Seven Excellence pH meter, Mettler-Toledo, Ltd.
Nuclear magnetic resonance (NMR)	JEOL ECZ-600
Electron impact ionization-mass spectrometry (EI-MS)	JEOL JMS-Q1500
Electrospray ionization-mass spectrometry (ESI-MS)	Shimadzu LC2010cHT and a Shimadzu LCMS-2020

2. Fabrication and operation of the OFET

Fabrication of the OFET device

A glass substrate was treated with a piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 4:1$ (v/v)). On the treated glass substrate, an Al gate electrode (30 nm in thickness) was formed through thermal deposition along with a shadow mask. An RIE apparatus was applied to activate the surface of the Al gate electrode. After obtaining a gate dielectric layer (AlOx), the surface of the glass substrate was fully covered with a fluorinated polymer material (CYTOP™ (CLT-809 in CT-Solv. 180, ratio 1:1 (v/v))) by a spin-coat method. An annealing process for the glass substrate was performed in an inert atmosphere glovebox (UNICO, UL-1300A-MSP) at 110 °C for 10 min. Next, the RIE treatment was carried out using a shadow mask to form a hydrophobic bank layer made of CYTOP™ through an etching process. To form a self-assembled monolayer-based dielectric layer on the AlOx layer, the device was immersed in a 2-propanol solution containing TDPA (10 mM) for 15 h at 25 °C. The treated device was rinsed with 2-propanol and dried with N_2 gas, followed by annealing at 110 °C for 30 min. After this period, an Au layer (30 nm in thickness) was deposited to form the source and drain electrodes. Subsequently, 1,2-dichlorobenzene solution containing PBTTC-C14 (0.0075wt%) was drop cast onto the channel region (width: 1000 μm , length: 50 μm). After baking at 160 °C for 10 min, an organic semi-conductive layer was obtained. Finally, the CYTOP™ solution was spin-coated on the entire surface of the device and annealed at 110 °C for 10 min.^{S1, S2}

Operation of the OFET device

Basic device characteristics (Fig. S1(a) transfer and (b) output) were measured under ambient conditions. The transfer characteristics were recorded by scanning gate voltages ($V_{\text{GS}} = 0.5$ to -3 V) at a certain drain-source voltage ($V_{\text{DS}} = -2$ V). The output characteristics were measured at $V_{\text{DS}} = 0$ to -3 V at each V_{GS} condition ($V_{\text{GS}} = 0$ to -3 V, step: -1 V).

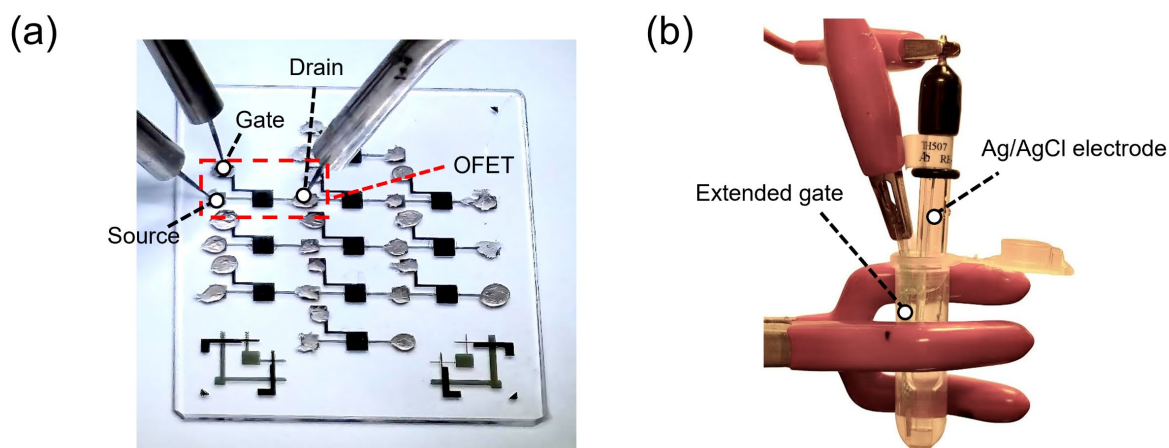


Fig. S1 Photographs of (a) the fabricated OFET device and (b) the detection portion.

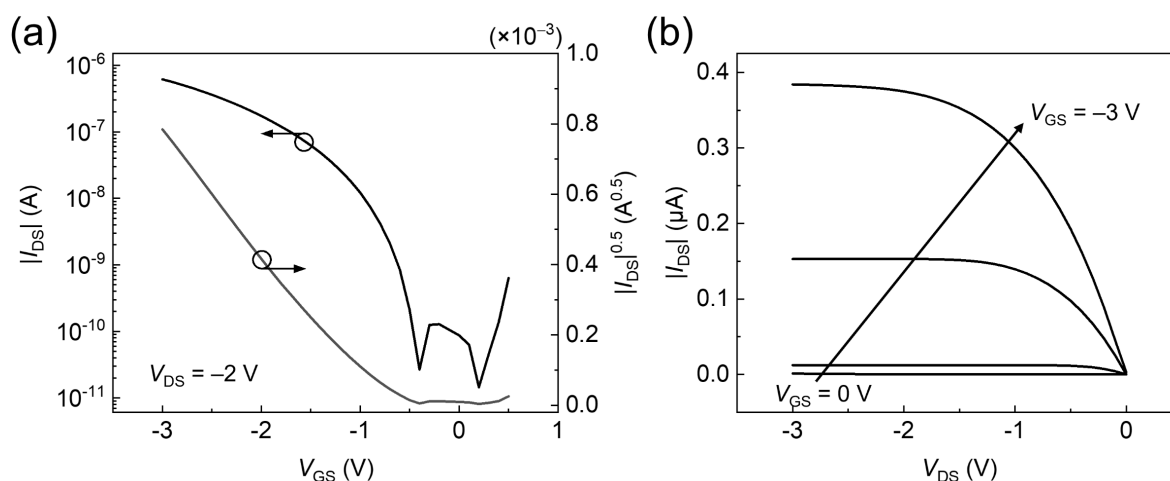


Fig. S2 (a) Transfer curve ($I_{DS} - V_{GS}$) at $V_{DS} = -2$ V and (b) output curves ($I_{DS} - V_{DS}$) at $V_{GS} = 0 - -3$ V.

3. Fabrication and characterization of the extended-gate Au electrode

Fabrication of the extended-gate Au electrode

An extended-gate Au electrode (15 mm² for functionalization area, 100 nm in thickness) was thermally deposited on the PEN film. A metal mask was used for patterning. The surface of the extended-gate Au electrode was rinsed with methanol before SAM modification. The extended-gate electrode was immersed in a methanol solution containing EMT (1 mM) and TCEP (5 mM) at 25 °C for 60 min. After this period, the surface of the electrode was gently washed with ethanol and dried with N₂ gas.

Linear sweep voltammetry (LSV)

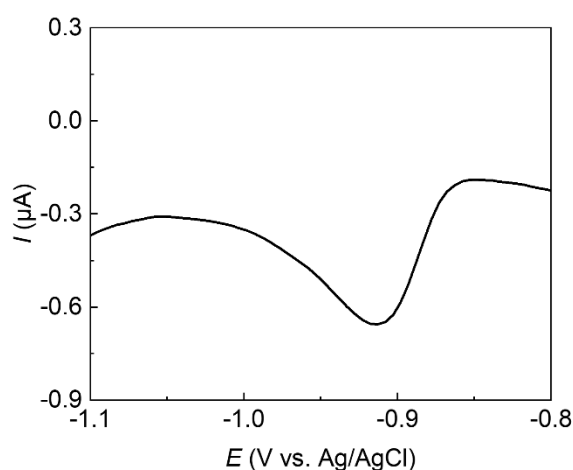


Fig. S3 Linear sweep voltammetry to estimate the molecular density of EMT on the extended-gate Au electrode (evaluated area: 15 mm²). The electrochemical measurement was performed in a KOH solution (0.1 M) with three repetitive measurements from 0 V to -1.2 V at 10 mV/s as the scan rate. Faraday's law with the integration of the peak area was applied to determine the molecular density.

Photoelectron yield spectroscopy (PYS) in air

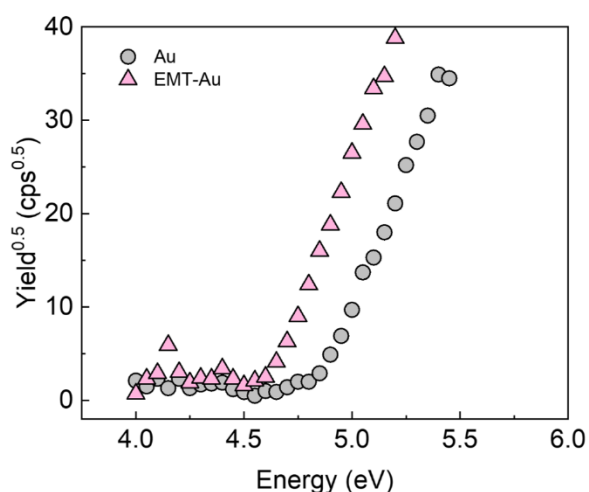


Fig. S4 PYS measurements of the extended-gate Au electrode before (grey circle, 4.89 ± 0.04 eV) and after functionalization of EMT (pink triangle, 4.76 ± 0.02 eV).

Contact angle measurements

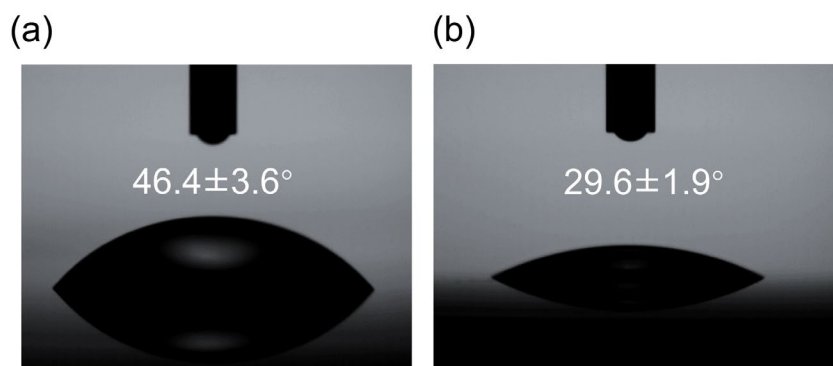


Fig. S5 Contact angles of water droplets on the extended-gate Au electrode (a) before ($46.4\pm 3.6^\circ$) and (b) after functionalization of EMT ($29.6\pm 1.9^\circ$) ($n = 3$).

X-ray photoelectron spectroscopy (XPS)

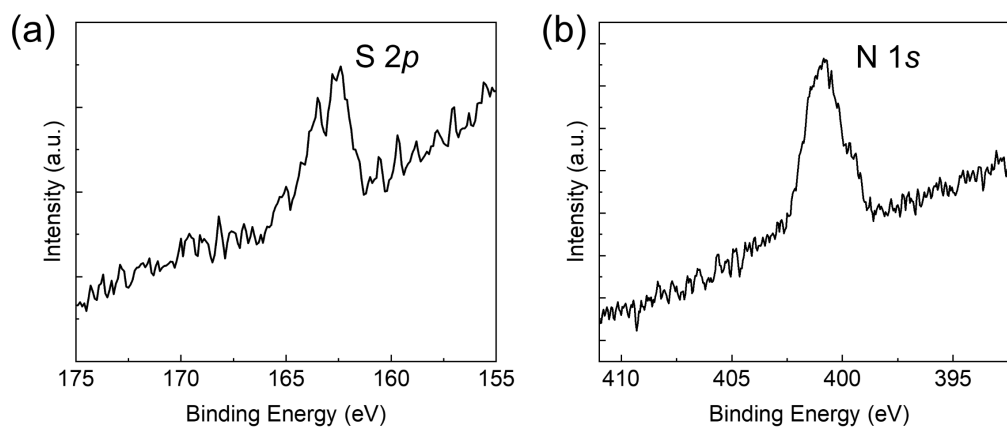


Fig. S6 XPS core-level spectra of (a) S 2p and (b) N 1s derived from the EMT-modified Au electrode.

4. Time-dependency test

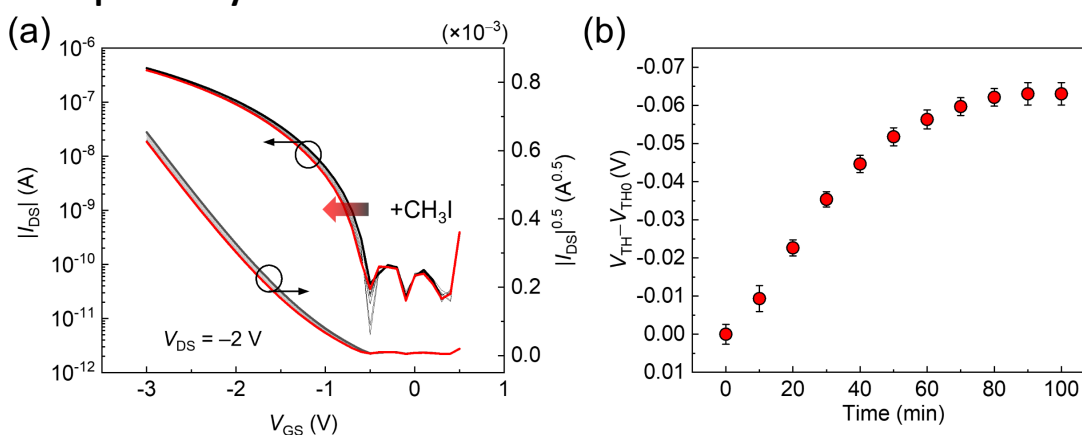


Fig. S7 (a) Time-dependent changes in the transfer characteristics of the EMT-attached OFET upon adding CH_3I ($100 \mu\text{M}$) in 100 mM HEPES buffer with 100 mM NaCl at pH 7.4. (b) The titration isotherm obtained by collecting V_{TH} at each measurement time from 0 to 100 min. The terms V_{TH0} and V_{TH} , respectively, indicate threshold voltages before and after adding CH_3I . Three repetitive evaluations were carried out for each measurement time.

5. Synthesis and identification of an alkylated EMT derivative

Synthesis and ^1H NMR analysis

1-Hydroxyethyl-5-methylthio-1H-tetrazole: EMT (44.5 mg, 0.304 mmol) was dissolved in 2-propanol (10 mL) in a round bottom flask. Iodomethane (213 mg, 1.50 mmol) was added to the solution and refluxed at 80°C for 15 h. After the removal of the solvent *in vacuo*, the product was dried at 60°C for 3 days under vacuum conditions (quant.). ^1H NMR (600 MHz, methanol- d_4): δ (ppm) 4.40 (t, 2H, $J = 5.1 \text{ Hz}$), 3.94 (t, 2H, $J = 5.7 \text{ Hz}$), 2.77 (s, 3H). MS (EI, +) m/z : 160 [EMT-H+ CH_3] $^{+}$.

Reaction of 1-hydroxyethyl-5-methylthio-1H-tetrazole and CH_3I in a solution: Iodomethane (64.8 g, 482 mmol) was mixed with 1-hydroxyethyl-5-methylthio-1H-tetrazole (48.7 mg, 304 μmol) without adding other solvents. After refluxing for 4 days, iodomethane was removed *in vacuo*. The residue was identified by ^1H NMR, ^1H - ^1H COSY, ^1H - ^{13}C HMQC, ^1H - ^{13}C HMBC, and ESI-MS analyses.

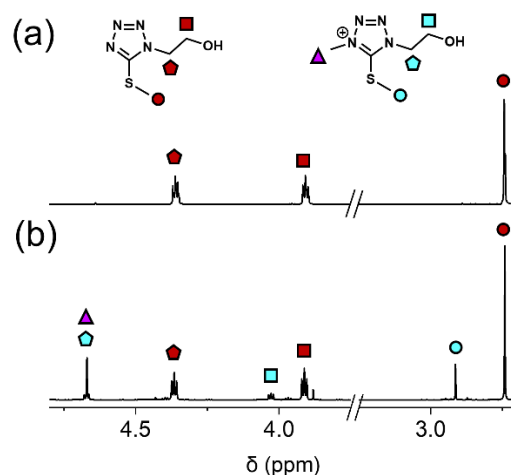


Fig. S8 ^1H NMR spectra (600 MHz, $\text{MeOH-}d_4$) of (a) 1-hydroxyethyl-5-methylthio-1H-tetrazole and (b) a mixture of 1-hydroxyethyl-5-methylthio-1H-tetrazole and CH_3I after the reaction.

ESI-MS analysis

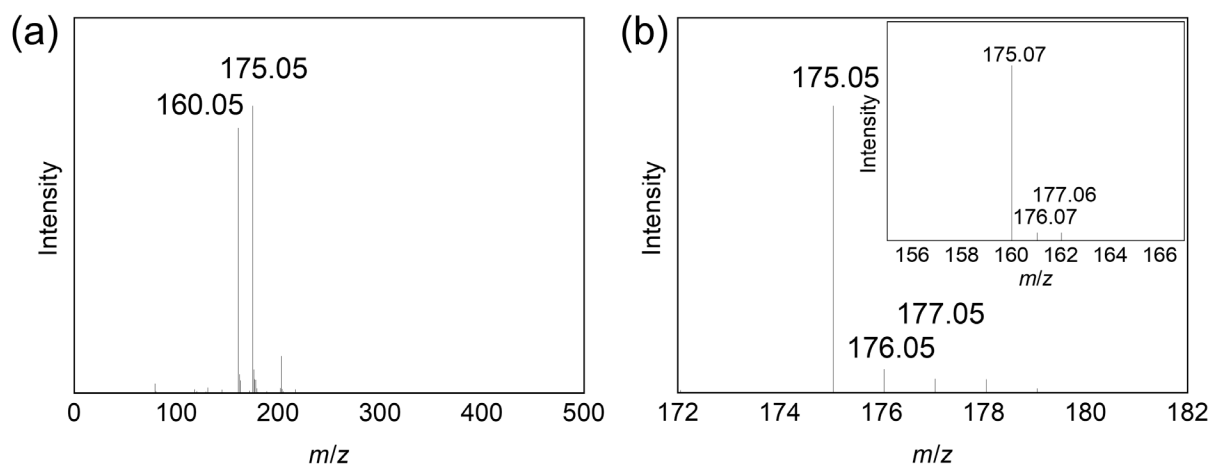


Fig. S9 ESI-MS spectra for a mixture of 1-hydroxyethyl-5-methylthio-1H-tetrazole and CH_3I after the reaction in MeOH. (a) A wide range of MS spectrum. (b) MS (ESI, +) m/z : $[\text{M}+\text{CH}_3]^+$, Calcd. for $\text{C}_5\text{H}_{11}\text{N}_4\text{OS}^+$ 175.07; Found: 175.05.

6. Selectivity test

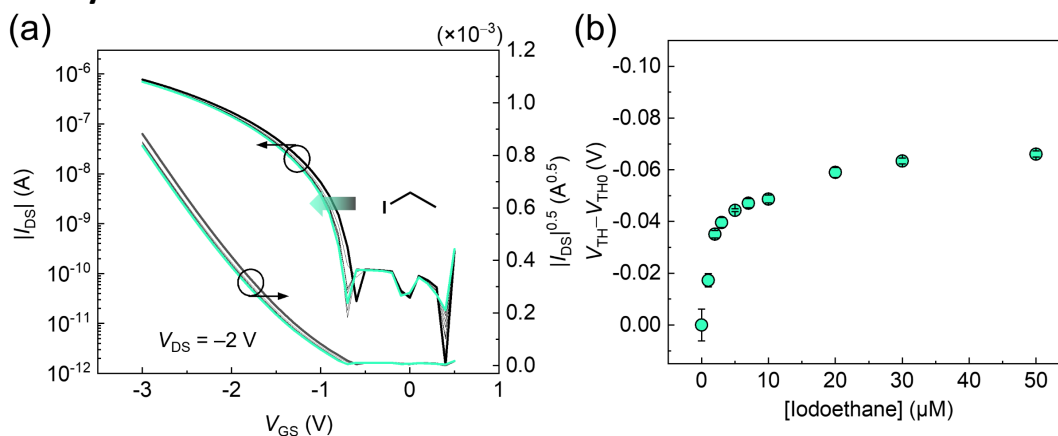


Fig. S10 (a) Transfer characteristics of the EMT-attached OFET upon adding $\text{CH}_3\text{CH}_2\text{I}$ in 100 mM HEPES buffer with 100 mM NaCl at pH 7.4. (b) The titration isotherm obtained by collecting V_{TH} at each concentration of $\text{CH}_3\text{CH}_2\text{I}$ from 0 to 50 μM . The terms V_{TH0} and V_{TH} , respectively, indicate threshold voltages before and after adding $\text{CH}_3\text{CH}_2\text{I}$.

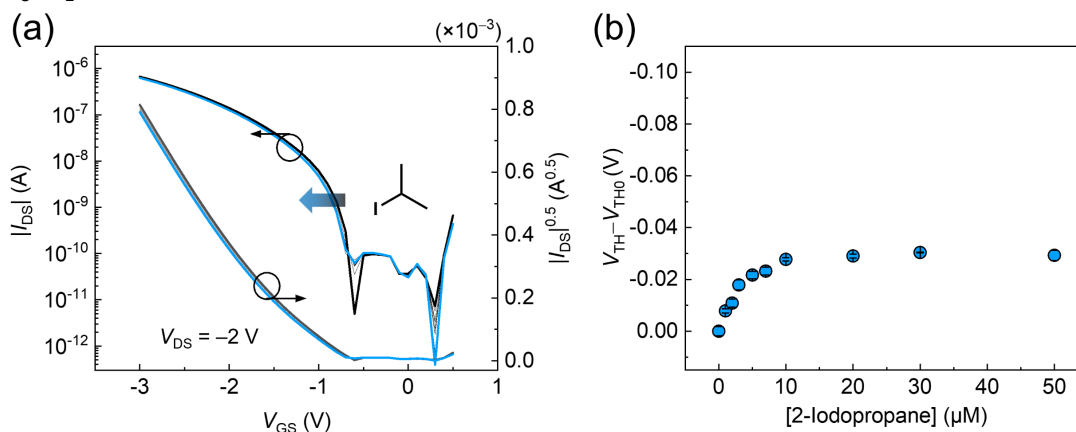


Fig. S11 (a) Transfer characteristics of the EMT-attached OFET upon adding $(\text{CH}_3)_2\text{CH-I}$ in 100 mM HEPES buffer with 100 mM NaCl at pH 7.4. (b) The titration isotherm obtained by collecting V_{TH} at each concentration of $(\text{CH}_3)_2\text{CH-I}$ from 0 to 50 μM . The terms V_{TH0} and V_{TH} , respectively, indicate threshold voltages before and after adding $(\text{CH}_3)_2\text{CH-I}$.

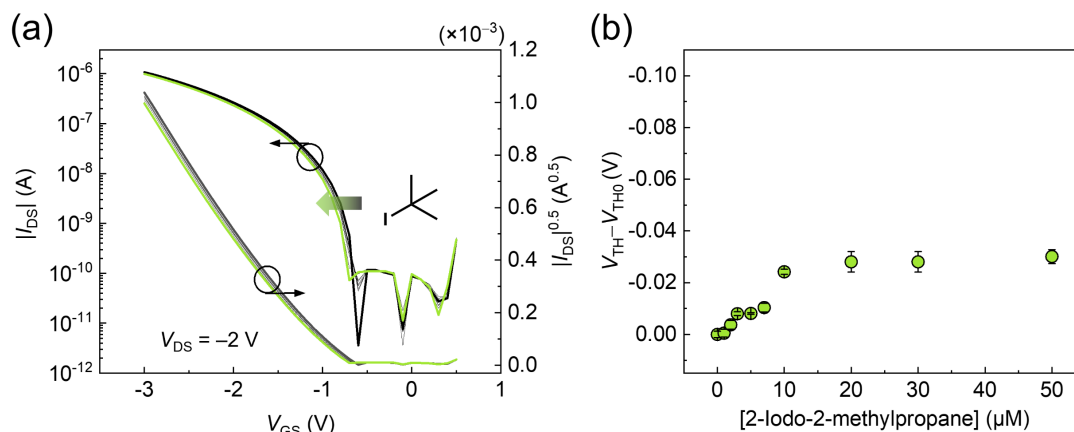


Fig. S12 (a) Transfer characteristics of the EMT-attached OFET upon adding $(\text{CH}_3)_3\text{C-I}$ in 100 mM HEPES buffer with 100 mM NaCl at pH 7.4. (b) The titration isotherm obtained by collecting V_{TH} at each concentration of $(\text{CH}_3)_3\text{C-I}$ from 0 to 50 μM . The terms V_{TH0} and V_{TH} , respectively, indicate threshold voltages before and after adding $(\text{CH}_3)_3\text{C-I}$.

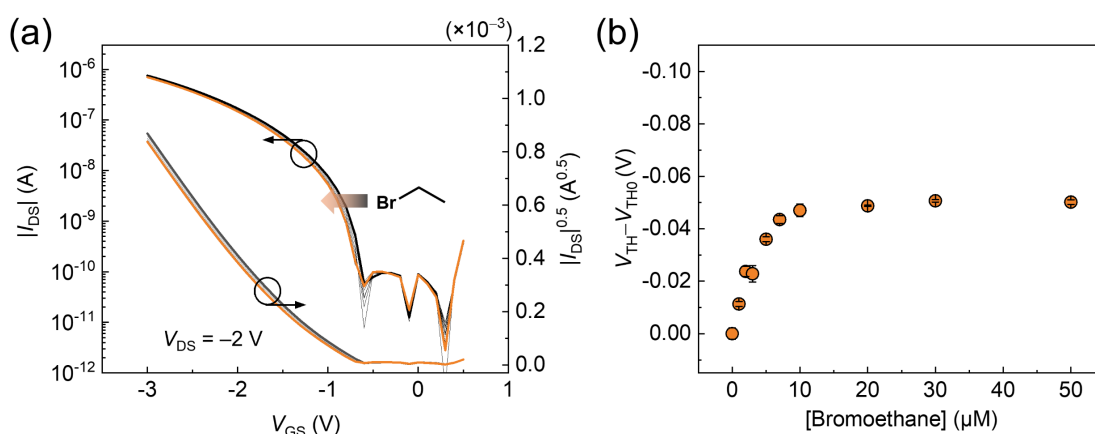


Fig. S13 (a) Transfer characteristics of the EMT-attached OFET upon adding $\text{CH}_3\text{CH}_2\text{Br}$ in 100 mM HEPES buffer with 100 mM NaCl at pH 7.4. (b) The titration isotherm obtained by collecting V_{TH} at each concentration of $\text{CH}_3\text{CH}_2\text{Br}$ from 0 to 50 μM . The terms V_{TH0} and V_{TH} , respectively, indicate threshold voltages before and after adding $\text{CH}_3\text{CH}_2\text{Br}$.

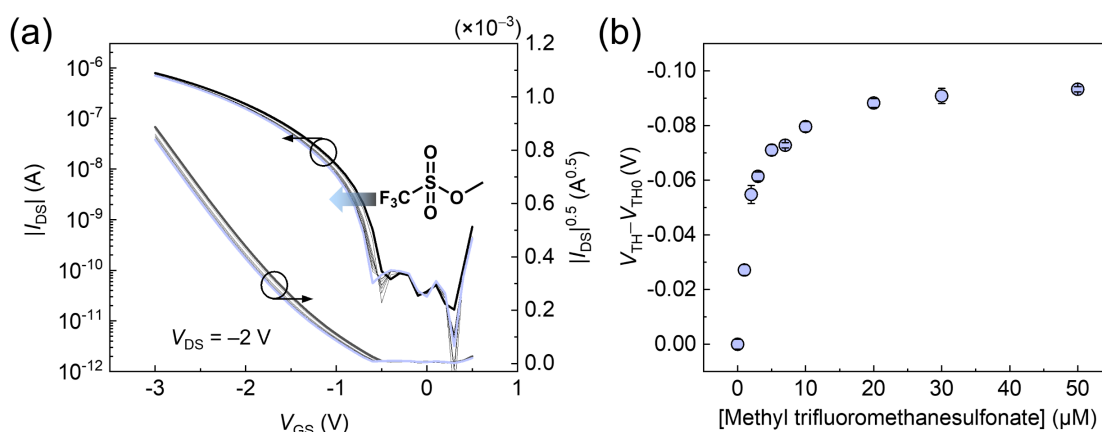


Fig. S14 (a) Transfer characteristics of the EMT-attached OFET upon adding $\text{CF}_3\text{SO}_3\text{CH}_3$ in 100 mM HEPES buffer with 100 mM NaCl at pH 7.4. (b) The titration isotherm obtained by collecting V_{TH} at each concentration of $\text{CF}_3\text{SO}_3\text{CH}_3$ from 0 to 50 μM . The terms V_{TH0} and V_{TH} , respectively, indicate threshold voltages before and after adding $\text{CF}_3\text{SO}_3\text{CH}_3$.

7. Semi-quantitative assay

The transfer characteristics at each electrophile concentration were measured with three repetitions for PCA. The inset data contained normalized drain currents (i.e., $|(I_{DS}-I_{DS0})/I_{DS}|$, at $V_{GS} = -1$ to -3 V), where I_{DS0} and I_{DS} represent the drain current before and after adding electrophiles. We constructed PCA with a Python platform with scikit-learn. Principal components (PC) are orthogonal eigenvectors that locate in the direction of the maximum variance within the inset data.^{S3} The order of contribution in variance during feature reduction is described as PC1 and PC2 constructed by shifts in I_{DS} .

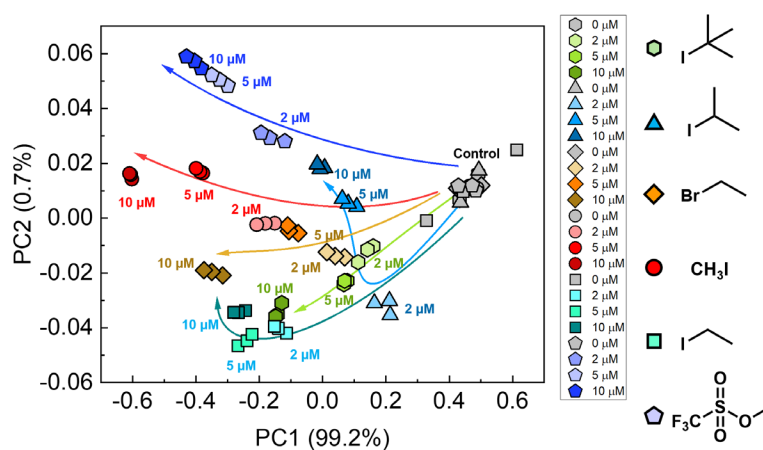


Fig. S15 PCA plot for the response patterns of six electrophiles at different concentrations (0, 2, 5, and 10 μ M).

References

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