Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information

An anion sensor based on an organic field effect transistor

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General

Reagents and solvents used for this study were commercially available and used as supplied. Cytop® (CTL-809M), PEN film, poly{2,5-bis(3-hexadecylthiophene-2-yl)thieno[3,2-*b*]thiophene},[1] gold, aluminum, FC-43 fluorinert, Teflon® AF1600, MES, and tetradecylphosphonic acid were purchased from Asahi Glass Co. Ltd., Teijin DuPont Films, Merck KGaA, Tanaka Kikinzoku Kogyo, Furuuchi Chemical Co., 3M Co., Dupont, Dojindo Laboratories, and Sigma–Aldrich Inc., respectively. Potassium fluoride, potassium bromide, potassium chloride, potassium dihydrogenphosphate, sodium chloride, and DMF were purchased from Kanto Kagaku. 1,2-Dichlorobenzene, potassium acetate, and 3-carboxy-5-nitrophenylboronic acid were purchased from Wako. 2-Aminoethanethiol, *N,N*-diisopropylethylamine, and PyBOP were purchased from TCI. The MES buffer solutions were prepared using Milli-Q water (18 MΩ cm at 25 ºC).

Metal electrodes were deposited by using a vacuum evaporator equipment from Cryovac, Co. An oxygen-plasma treatment was performed on a PC-300 plasma cleaners from Samco, Inc. UV ozone treatment was by a UV253H UV ozone cleaner from Filgen, Inc. The bank layers were prepared using an IMAGEMASTER 350 dispenser equipment from Musashi Engineering, Inc. Photoelectron spectroscopy measurements in air were performed using an AC-3 from Riken Keiki, Co. Wettability measurements were performed on a Theta T200 contact angle goniometer from Biolin Scientific, Co. X-ray photoelectron spectroscopy was measured by an ULVAC PHI-5600 spectrometer from ULVAC-PHI, Inc. The pH values of solutions were measured by a D-51 pH meter (Horiba, Ltd.). The Ag/AgCl electrode as the reference electrode was purchased from

BAS, Inc. The electrical characteristics of the all OFET devices were measured using a Keithley 2636B source meter.

Fabrication of the OFET device

An aluminum (Al) gate electrode was deposited onto a glass substrate (Eagle® XG, Corning) by thermal evaporation (30 nm in thickness). To achieve the low-voltage operation, the gate dielectric consisted of a thin-film of aluminum oxide layer (5 nm in thickness) and a tetradecylphosphonic acid-SAM (1.7 nm in thickness).[2] The aluminium-oxide layer was formed with an oxygen-plasma treatment of the Al gate electrode, whereby the plasma power was 300 W and the treatment duration was 50 min. The SAM treatment was performed by immersing the substrate in a 2-propanol solution of tetradecylphosphonic acid at room temperature. The gold (Au) source-drain electrodes (30 nm in thickness) were deposited onto the gate dielectric layer using thermal evaporation and patterned using a shadow mask. The channel width and length for the resulting OFET device were 1000 and 50 μm, respectively. To prepare the bank layers, a 1 wt% solution of an amorphous fluoropolymer in FC-43 was applied using the dispenser equipment. Subsequently, a semiconducting polymer, pBTTT-C_{16} was drop-casted from a 0.03 wt% solution of 1,2-dichlorobenzene, and then annealed at 175 ˚C for 30 min in a nitrogen atmosphere. To passivate the completed device, Cytop® (CTL-809M) was applied by spin-coating and baked at 100 ˚C for 10 min. (100 nm in thickness). Finally, an extended-gate electrode consisting of Au was prepared on a PEN film substrate (125 μm in thickness) using thermal evaporation, whereby the sensing area for the extended-gate electrode was 15 mm^2.

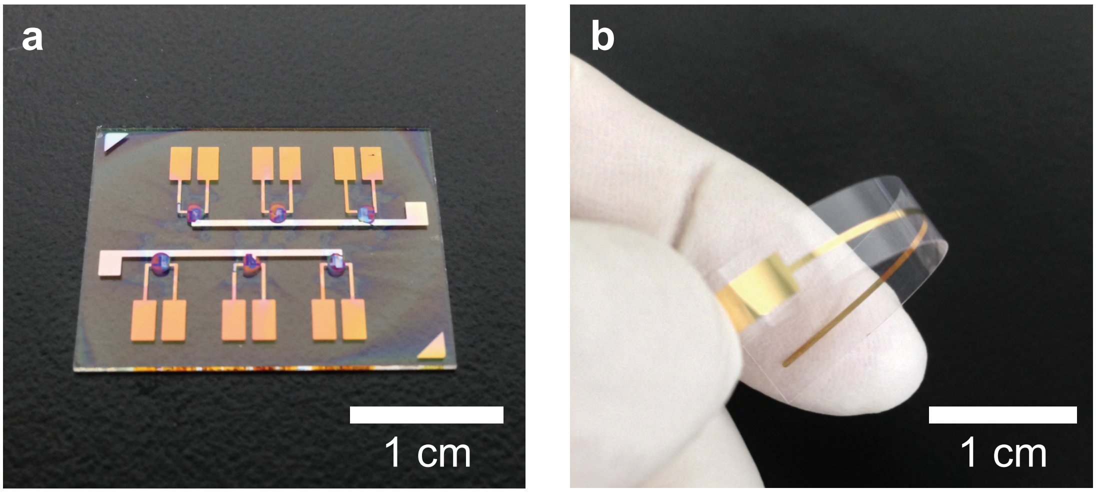
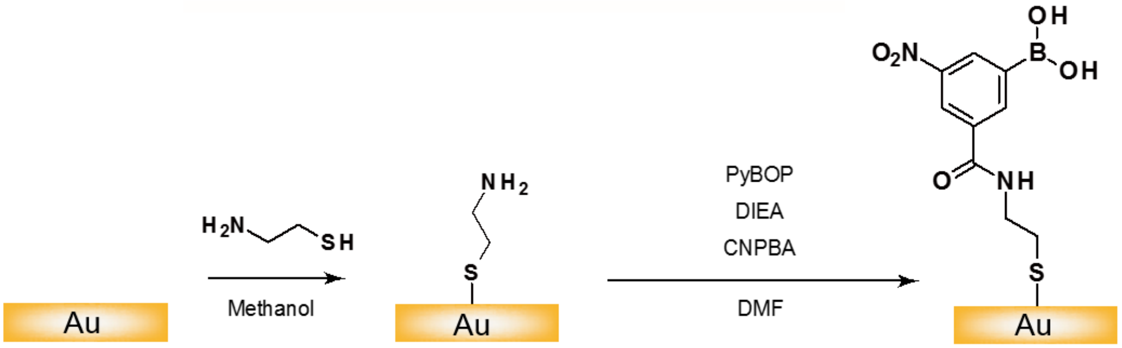


Fig. S1. Photographs of (a) the OFET devices and (b) the detection portion (i.e. the extended-gate electrode).

Functionalization of the extended-gate electrode

The Au extended-gate electrode was immersed in a methanol solution containing 10 mM of 2-aminoethanethiol for 1 h at room temperature to form an AET-SAM layer. The treated electrode was then rinsed with ethanol and water, after which 5 µL of a *N, N*-dimethylformamide (DMF) containing 3-carboxy-5-nitrophenylboronic acid (CNPBA, 5 mM), benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP, 8.3 mM), and *N,N*-diisopropylethylamine (15 mM) was applied to the electrode in drops. The reaction time for the amide formation was for 7 h at room temperature, after which the electrode was rinsed with DMF, ethanol and water.



Scheme S1. Functionalization of the extended-gate electrode.

Electric characteristics of the OFET

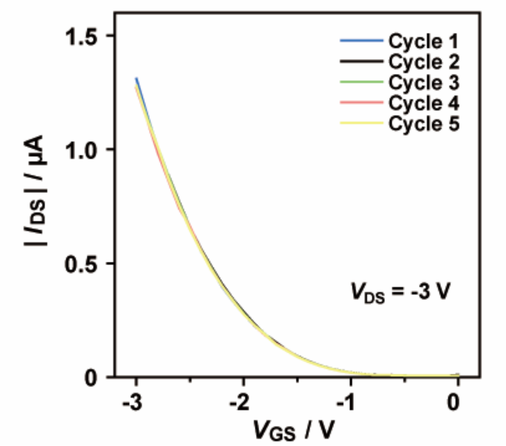


Fig. S2. Repetitive measurements of the transfer characteristics of the fabricated OFET device.

The relationship of drain currents and threshold voltages

To estimate threshold voltages, the following equation[3] was used:

$$I_{DS} = \frac{W}{2L}\mu C(V_{GS} - V_{TH})^2$$

where I_{DS} is the drain current, W and L are the channel width and length, μ is the field-effect mobility, C is the capacitance of the gate dielectric (0.8 μF/cm^2)[4], V_{GS} is the gate voltage, and V_{TH} is the threshold voltage.

Anion titrations

For the detection of anion species, an extended-gate electrode functionalized with PBA was immersed in a MES buffer solution containing F^-, Cl^-, Br^-, $H_2PO_4^-$, or AcO^- (0-50 mM) with 100 mM NaCl at room temperature, after which anions were electrically detected by the OFET.

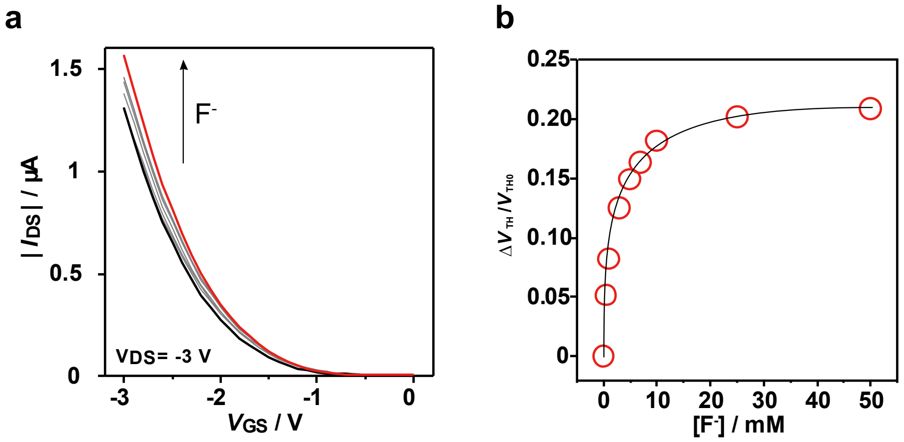


Fig. S3. (a) Transfer characteristics (I_{DS}-V_{GS}) of the OFET device upon titration with F^- in a MES buffer solution (100 mM) at pH 5.5 at room temperature. (b) Changes in threshold voltage for the OFET devices by F^- at various concentrations in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. [Fluoride] = 0-50 mM.

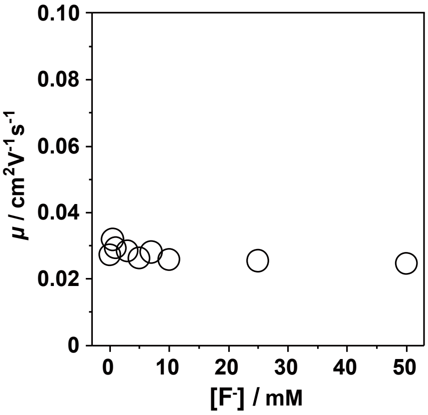


Fig. S4. The field-effect mobility of the OFET upon titration with fluoride in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. [Fluoride] = 0-50 mM.

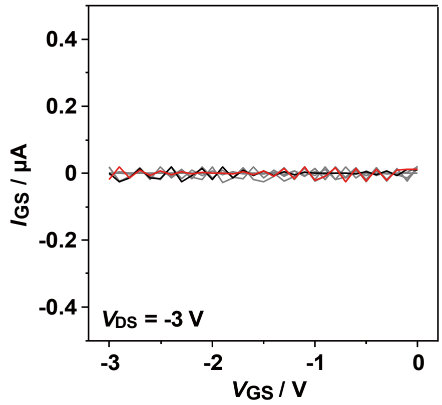


Fig. S5. The gate-source current (I_{GS}-V_{GS}) of the OFET upon titration with fluoride in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. [Fluoride] = 0-50 mM.

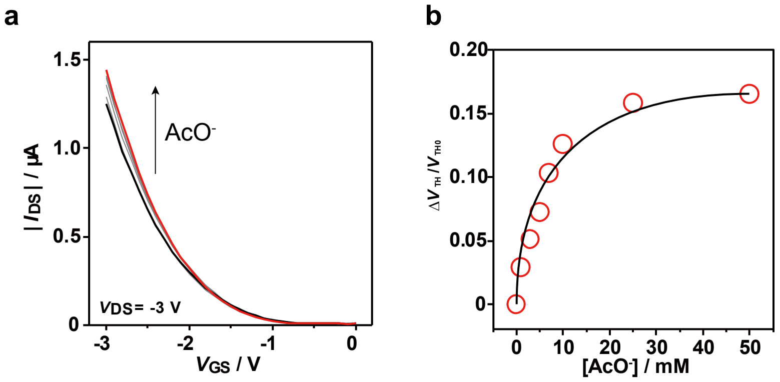


Fig. S6. (a) Transfer characteristics (I_{DS}-V_{GS}) of the OFET device upon titration with AcO$^-$ in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. (b) Changes in threshold voltage for the OFET devices by AcO$^-$ at various concentrations in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. [AcO$^-$] = 0-50 mM.

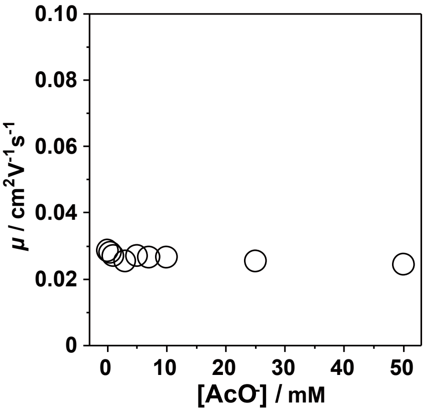


Fig. S7. The field-effect mobility of the OFET upon titration with AcO$^-$ in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. [AcO$^-$] = 0-50 mM.

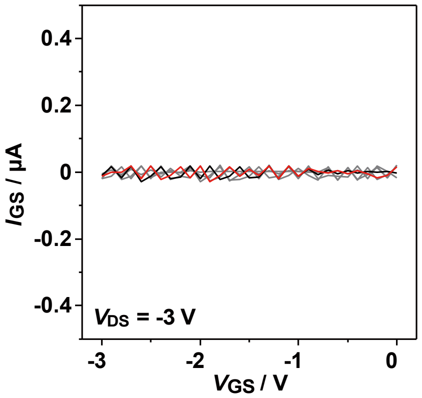


Fig. S8. The gate-source current (I_{GS}-V_{GS}) of the OFET upon titration with AcO^- in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. [AcO^-] = 0-50 mM.

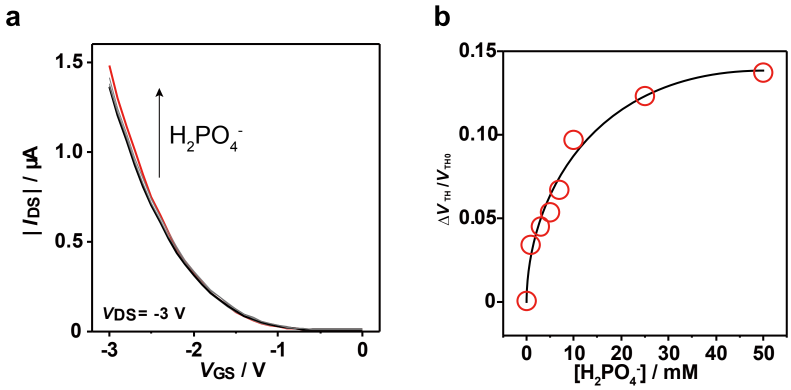


Fig. S9. (a) Transfer characteristics (I_{DS}-V_{GS}) of the OFET device upon titration with $H_2PO_4^-$ in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. (b) Changes in threshold voltage for the OFET devices by $H_2PO_4^-$ at various concentrations in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. [$H_2PO_4^-$] = 0-50 mM.

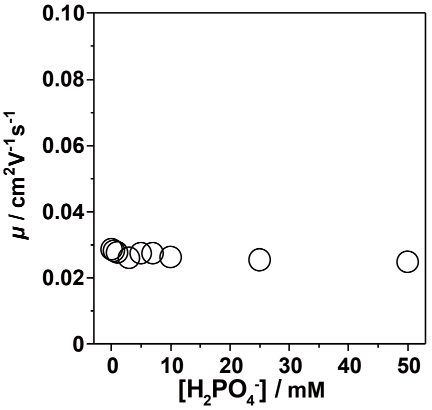


Fig. S10. The field-effect mobility of the OFET upon titration with $H_2PO_4^-$ in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. [$H_2PO_4^-$] = 0-50 mM.

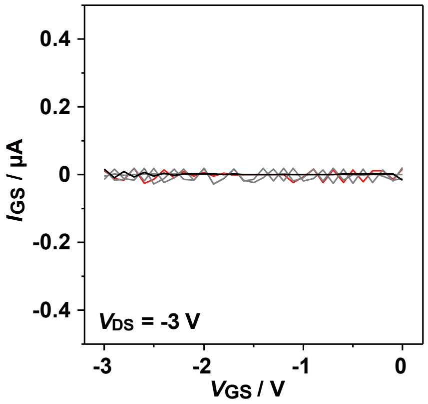


Fig. S11. The gate-source current (I_{GS}-V_{GS}) of the OFET upon titration with $H_2PO_4^-$ in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. [$H_2PO_4^-$] = 0-50 mM.

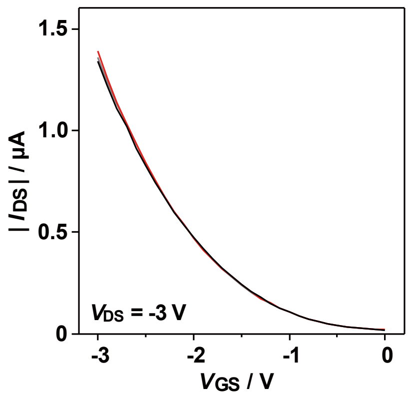


Fig. S12. Transfer characteristics (I_{DS}-V_{GS}) of the OFET device upon titration with Cl^- in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. [Chloride] = 0-50 mM.

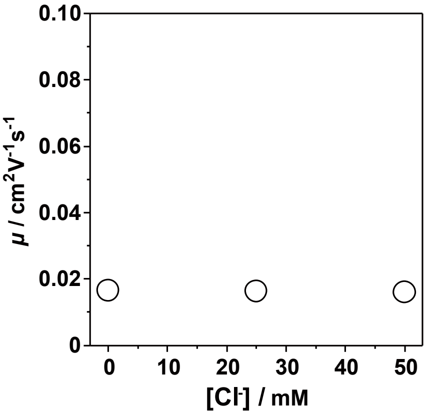


Fig. S13. The field-effect mobility of the OFET upon titration with Cl^- in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. [Chrolide] = 0-50 mM.

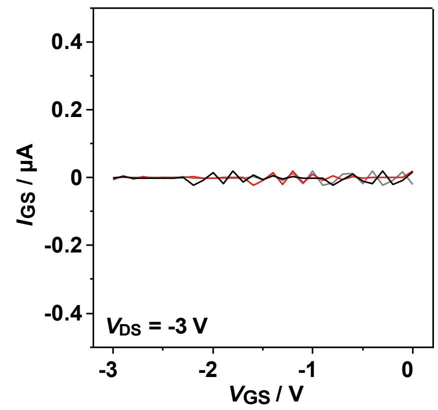


Fig. S14. The gate-source current (I_{GS}-V_{GS}) of the OFET upon titration with Cl^- in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. [Chloride] = 0-50 mM.

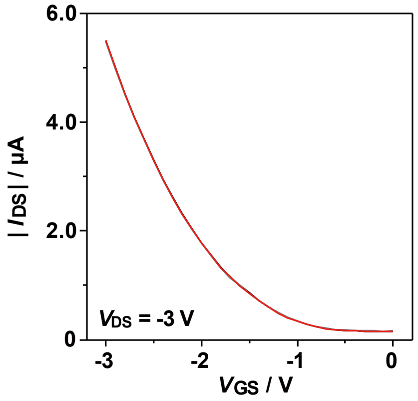


Fig. S15. Transfer characteristics (I_{DS}-V_{GS}) of the OFET device upon titration with Br^- in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. [Bromide] = 0-50 mM.

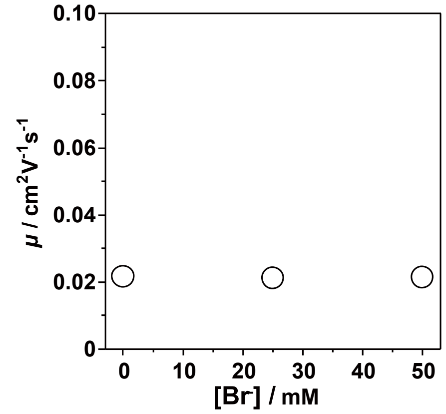


Fig. S16. The field-effect mobility of the OFET upon titration with Br^- in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. [Bromide] = 0-50 mM.

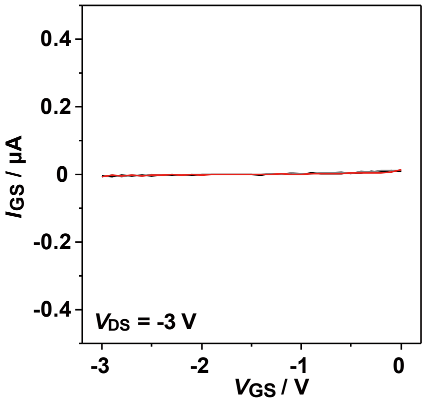


Fig. S17. The gate-source current (I_{GS}-V_{GS}) of the OFET upon titration with Br^- in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at room temperature. [Bromide] = 0-50 mM.

References

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