Supporting Information

Antibody- and Label-Free Phosphoprotein Sensor Device Based on an Organic Transistor

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General

Reagents and solvents employed for this study were used as supplied. Cytop (CTL-809M), PEN film, poly{2,5-bis(3-hexadecylthiophene-2-yl)thieno[3,2-*b*]thiophene}, gold, aluminum, FC-43 fluorinert, Teflon AF1600, and tetradecylphosphonic acid were purchased from Asahi Glass Co. Ltd., Teijin DuPont Films, Merck KGaA, Tanaka Kikinzoku Kogyo, Furuuchi Chemical Co., 3M Co., Dupont, and Sigma–Aldrich Inc., respectively. Zinc nitrate hexahydrate and sodium chloride were purchased from Kanto Chemical Co. Inc. Phospho-α-casein, dephospho-α-casein and albumin were purchased from Wako Pure Chemical Industries, Ltd. Lysozyme and β-galactosidase were purchased from Sigma-Aldrich Inc. 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) was purchased from Dojindo Laboratories. The HEPES 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 (RE-1S) was purchased

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

Synthesis

2-(Bis(pyridine-2-yl-methyl)amino)ethane-1-thiol was synthesized according to a literature.[1] 2,2'-Dipicolylamine (3.11 g, 15.6 mmol) in benzene (3.1 mL) was placed in a round-bottom flask. Ethylene sulfide (1.86 mL, 31.2 mmol) in benzene (3.1 mL) was added dropwise and the mixture solution stirred at 65 ºC for 2 days under N_2 atmosphere. The resulting solution was evaporated and chromatographed on alumina (dichloromethane as an eluent). In this way, 1.11 g of the final product was obtained (29% yield). The identification data of the product were in agreement with the literature.[1]

Fabrication of the OFET Device

A gate electrode was deposited on a glass substrate by thermal evaporation (Al, 30 nm in thickness). The gate dielectric layer was constructed by the following surface treatment of the Al layer. The aluminum oxide (AlOx) layer was prepared by an oxygen-plasma treatment of the Al gate electrode. The duration of the oxygen-plasma treatment was 50 min and the plasma power was 300 W. Then, the SAM (self-assembled monolayer) treatment was carried out by immersing the substrate in a 1 mM tetradecylphosphonic acid in a 2-propanol solution at room temperature for 16 h. A gold was used as source-drain electrodes and thermally deposited on the gate dielectric layer through the shadow mask (30 nm in thickness). The channel width and length of the

device were 1000 and 50 μm, respectively. The bank layer comprises an amorphous fluoropolymer (a 1 wt% solution of Teflon AF1600) in FC-43) that was built by dispenser equipment. Afterward, to prepare the semiconducting layer, a 0.03 wt% solution of pBTTT (poly(2,5-bis(3-hexadecylthiophene-2-yl)thieno[3,2-*b*]thiophene)) in 1,2-dichlorobenzene was drop-casted into the bank layers, and then annealed at 150 ºC for 30 min in a nitrogen atmosphere. Subsequently, a passivation layer, Cytop (CTL-809M) was directly spin-coated on the substrate and baked at 100 ºC for 10 min (100 nm in thickness).

Modification of the Extended-Gate Electrode

An extended-gate electrode made of Au was prepared on a PEN (polyethylene naphthalate) film substrate (125 μm in thickness) using thermal evaporation, whereby the sensing area for the extended-gate electrode was 15 mm^2. The electrode was washed by ethanol and water, followed by immersion in the solution of 2-(bis(pyridine-2-yl-methyl)amino)ethane-1-thiol (DPA, 10 mM in a methanol solution) for 1 h at room temperature. The electrode was then rinsed with ethanol and pure water. The electrode was immersed in a HEPES buffer solution (10 mM, pH 7.4) containing $Zn(NO_3)_2$ (1 mM) for 1 h at room temperature. Finally, the extended-gate electrode was rinsed with pure water.

Electric Characteristics of the OFET

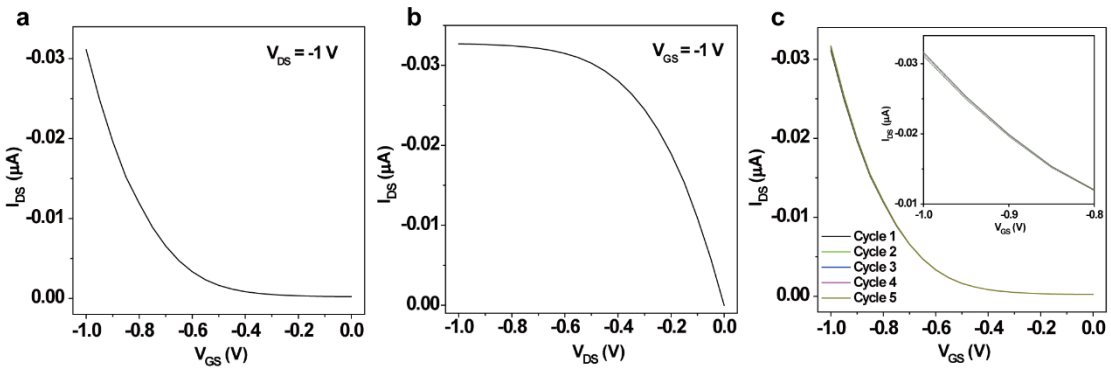

Figure S1. (a) Transfer and (b) output characteristics of the fabricated OFET device. (c) Transfer characteristics of the OFET under 1 V in several measurements.

Time-Dependency of Electrical Response to *α*-Casein

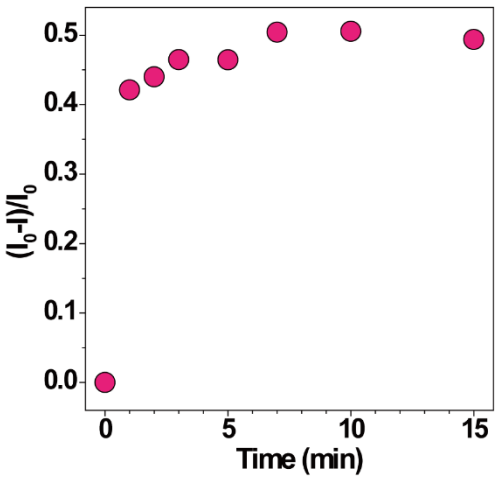

Figure S2. Time dependency of the electrical response to *α*-casein (6 µg/mL) in a HEPES buffer solution (10 mM) with NaCl (100 mM) at pH 7.4 at r.t.

Electric Detection of Proteins

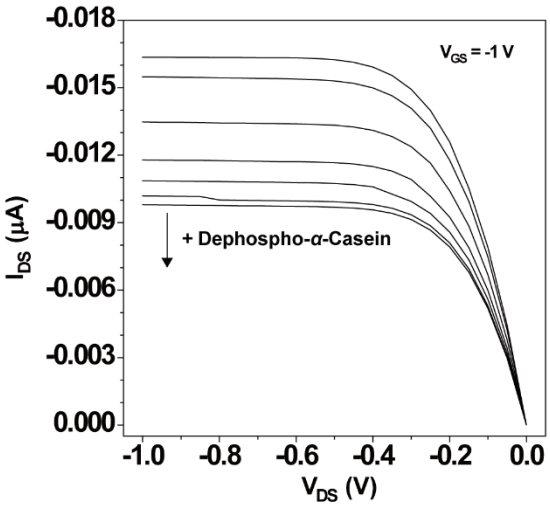

Figure S3. Output characteristics of the OFET upon addition of increased amounts of dephospho-α-casein in a HEPES buffer solution (10 mM) with NaCl (100 mM) at pH 7.4 at r.t. [Dephospho-α-casein] = 0–6 µg/mL.

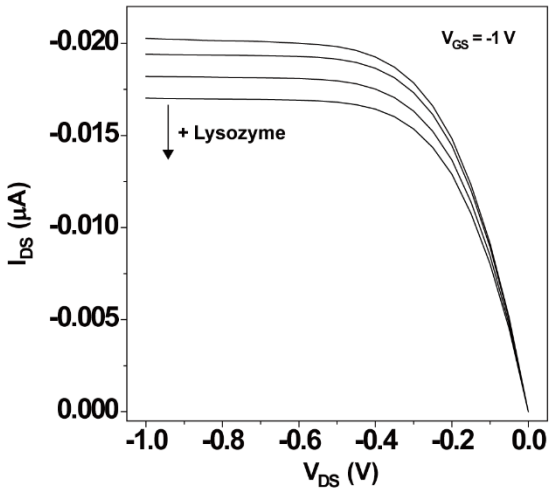

Figure S4. Output characteristics of the OFET upon addition of increased amounts of lysozyme in a HEPES buffer solution (10 mM) with NaCl (100 mM) at pH 7.4 at r.t. [Lysozyme] = 0–6 µg/mL.

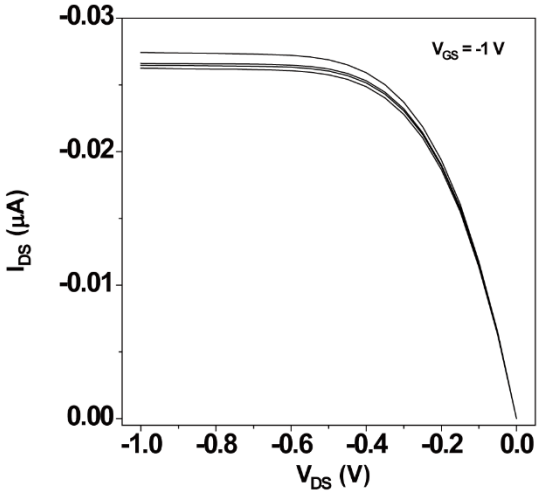

Figure S5. Output characteristics of the OFET upon addition of increased amounts of *β*-galactosidase in a HEPES buffer solution (10 mM) with NaCl (100 mM) at pH 7.4 at r.t. [*β*-Galactosidase] = 0–6 μg/mL.

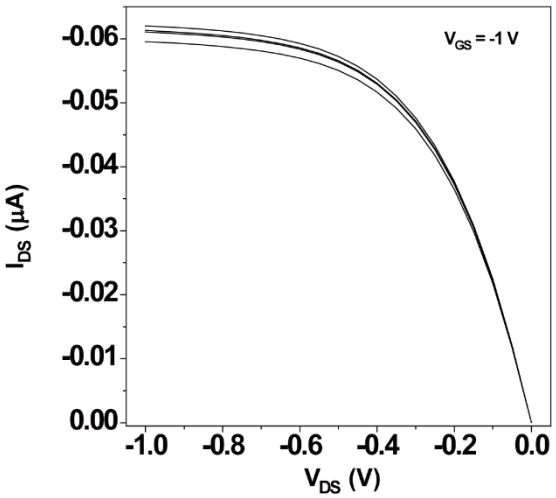

Figure S6. Output characteristics of the OFET upon addition of increased amounts of albumin in a HEPES buffer solution (10 mM) with NaCl (100 mM) at pH 7.4 at r.t. [Albumin] = 0–6 μg/mL.

Reference

(1) Lazarova, N.; Babich, J.; Valliant, J.; Schaffer, P.; James, S.; Zubieta, J. *Inorg. Chem.* **2005**, *44*, 6763–6770.