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Supplementary Information

A mercury (II) ion sensor device based on an organic field effect transistor with an extended-gate modified by dipicolylamine

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Contents

General

Reagents and solvents employed 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}, gold, aluminum, FC-43 fluorinert, Teflon® AF1600, HEPES, 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. Mercury nitrate monohydrate and 2,6-pyridinecarboxylic acid were purchased from Sigma-Aldrich Inc. Aluminum nitrate enneahydrate, calcium nitrate tetrahydrate, cobalt nitrate hexahydrate, magnesium nitrate hexahydrate, gallium nitrate n-hydrate, nickel nitrate hexahydrate, and copper nitrate hexahydrate were purchased from Wako Pure Chemical Industries, Ltd. Zinc nitrate hexahydrate and sodium chloride were purchased from Kanto Chemical Co. Inc. Ethylenediaminetetraacetic acid disodium salt was purchased from TCI. 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.). Variable angle spectroscopic ellipsometry measurements at seven incident angles from 45 ° to 75 ° in steps of 5 ° were performed on a M-2000U from J. A. Woollam Co., Inc. 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.

The details of the recovery experiment with an aqueous solution of EDTA are as follows: the extended-gate modified with the DPA was immersed in a HEPES buffer

solution (10 mM) including $Hg(NO_3)_2$ (3 μM) and NaCl (100 mM) for 10 min at pH 7.4 at r.t. After the electrical measurements of the OFET device were carried out, the electrode was rinsed with pure water. The electrode was then immersed in a HEPES buffer solution (10 mM) including EDTA (10 μM) and NaCl (100 mM) for 20 min at pH 7.4 at r.t. Subsequently, the electrode was immersed in a HEPES buffer solution (10 mM) with NaCl (100 mM) for 10 min at pH 7.4 at r.t. After this period, the electrical properties of the OFET were measured again by the 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

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). The aluminum-oxide layer was formed by 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 r.t. 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 a Teflon® AF1600 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 for 30 min at 150 ˚C in a nitrogen atmosphere. To passivate the completed device, Cytop® (CTL-809M) was applied by spin-coating and baked for 10 min at 100 ˚C (100 nm in thickness). Finally, an extended-gate electrode consisting 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.

Electric characteristics of the OFET

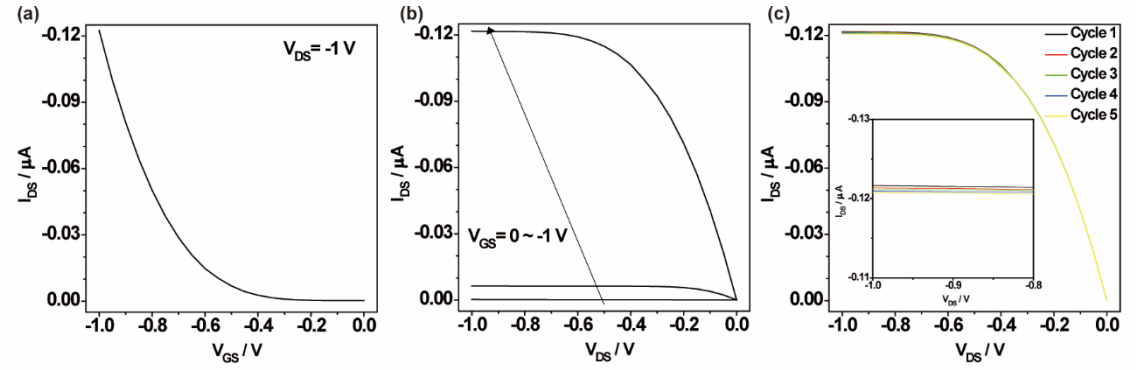

Fig. S1. (a) Transfer and (b) output characteristics of the fabricated OFET device. (c) Transfer characteristics of the OFET under 1 V in several measurements.

Modification and characterization of the extended-gate electrode

The Au extended-gate electrode was immersed in a methanol solution containing 10 mM of 2-(bis(pyridine-2-yl-methyl)amino)ethane-1-thiol for 1 h at r.t. The immersed electrode was then rinsed with ethanol and water.

We confirmed the modification of the extended-gate electrode with the thiolated DPA by photoelectron yield spectroscopy in air (PYS), surface wettability, X-ray photoelectron spectroscopy (XPS) and ellipsometry measurements. Firstly, the results of PYS showed a lower work function on the DPA-treated electrode (4.19 ± 0.04 eV) than the untreated Au electrode (4.65 ± 0.04 eV) (Fig. S2), which can be explained by an electron-donating functional group (*i.e.* DPA) covering the surface of the Au electrode. Next, water contact angles for the DPA-treated surface and the untreated Au one were 51 ± 3.8˚ and 45±1.7˚, respectively (Fig. S3). The slight increase in the surface wettability indicates that the hydrophobic group (*i.e.* DPA) was immobilized on the Au surface. Moreover, XPS revealed the presence of carbon, nitrogen, and sulfur with their expected binding energies (Fig. S4). Finally, the thickness of the DPA layer was estimated to be 1.1 nm (an assuming refractive index = 1.72) by using variable angle spectroscopic ellipsometry measurements at seven incident angles from 45˚ to 75˚ in steps of 5˚. Based on these results, we concluded the modification of the DPA on Au that was successfully accomplished.

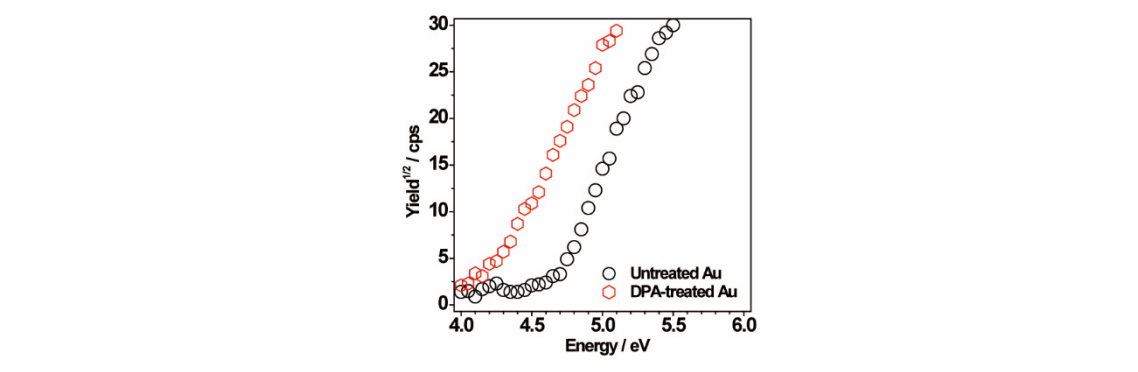

Fig. S2. Photoelectron yield spectroscopy measurements of the Au extended-gate electrode surfaces in air. Untreated Au (black circle), DPA-treated Au (red hexagon).

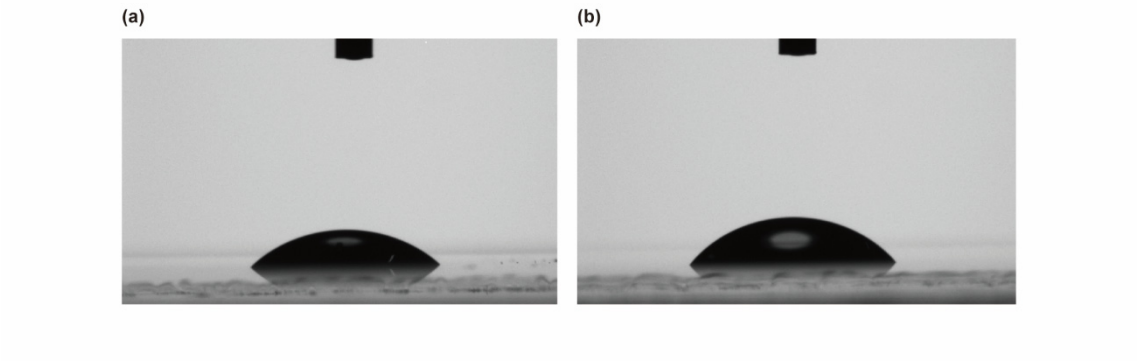

Fig. S3. Measurements of water contact angle on the Au extended-gate electrodes. (a) Untreated Au (b) DPA-treated Au.

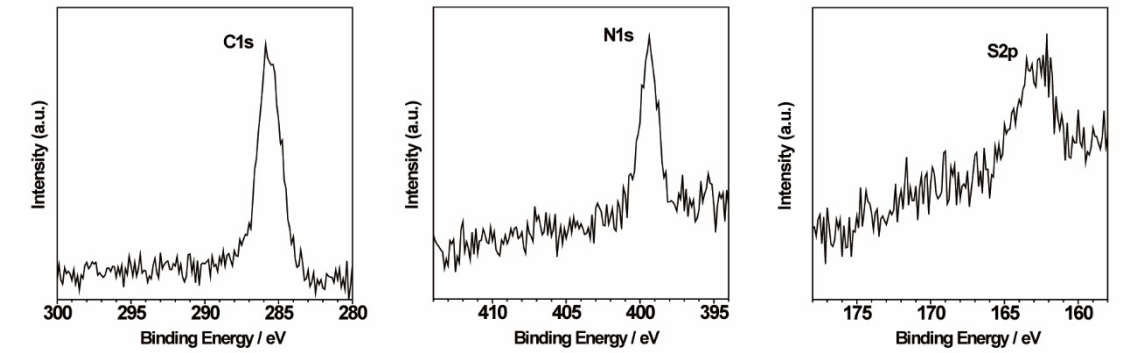

Fig. S4. XPS spectra of the C1s, N1s, and S2p regions of the DPA-treated Au.

Detection of metal ions

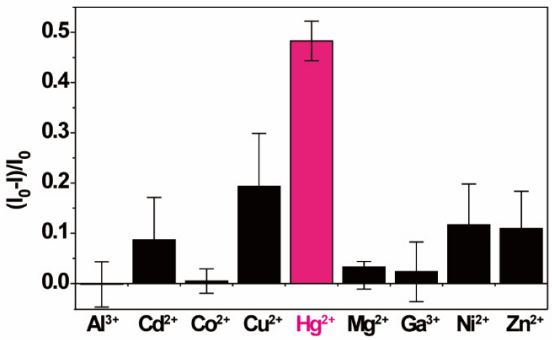

Fig. S5. Output current changes in the fabricated OFET sensor after adding of various metal ions in a HEPES buffer solution (10 mM) with NaCl (100 mM) at pH 7.4 at r.t. [Metal ion] = 3 μM. Three repetitions were measured for each analyte using the same device.

Competitive experiment for the Hg^{2+} detection

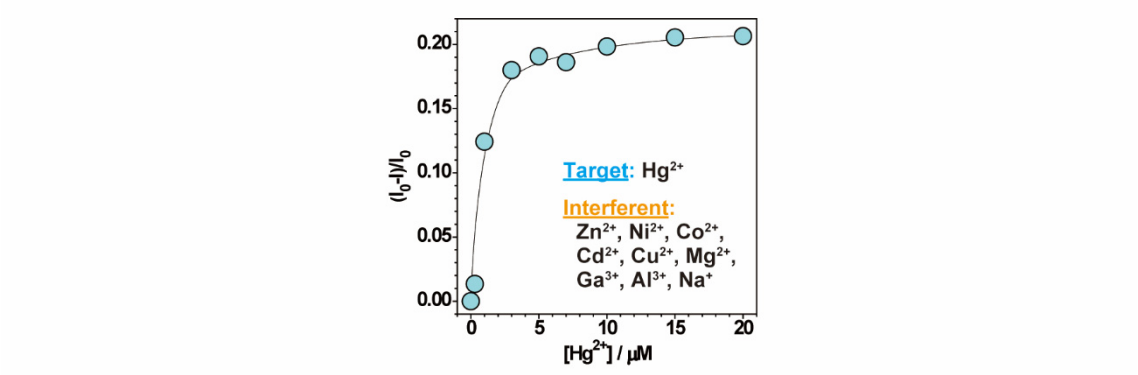

Fig. S6. Changes in the output current of the OFET by addition of Hg^{2+} at various concetratioins in a HEPES buffer solution (10 mM) with NaCl (100 mM) in the presence of interferent metal ions (Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Mg^{2+}, Ga^{3+}, and Al^{3+}) (each $[M^{n+}]$ = 3 μM) and PDCA (1 mM) at pH 7.4 at r.t.

Reference

1 N. Lazarova, J. Babich, J. Valliant, P. Schaffer, S. James and J. Zubieta, *Inorg. Chem.*, 2005, **44**, 6763.