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Anion sensor based on organic field effect transistor

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We propose an organic field effect transistor (OFET)-based sensor design as a new and innovative platform for anion detection. OFETs could be fabricated on low-cost plastic film substrates using printing technologies, suggesting that the OFETs can potentially be applied to practical supramolecular anion sensor devices in the near future.

It is widely acknowledged that the detection of anions is of great importance to environmental conservation as well as medicinal chemistry.¹ For example, excess fluoride (F⁻) causes crippling skeletal fluorosis in a number of areas of the world.² Also, phosphates are known cause of eutrophication. Furthermore, the control of signal transduction is attained by phosphate groups in phosphorylated proteins and lipids.³ In addition, the roles of carboxylates are very important in pharmaceutical field such as nonsteroidal anti-inflammatory drugs.⁴ Carboxylate drugs present a significant environmental burden because of their extensive use. Accordingly, the development of anion sensors is clearly of great importance.

The monitoring of anions in aqueous media is challenging because anions are not only larger than their isoelectronic cations, but they also exhibit various geometries and strong hydration.¹ Representative examples of anion-detectable chemosensors in aqueous systems are metal-ligand coordination,⁵ hydrogen-bonding⁶ and/or electrostatic interaction⁷ based anion-sensors. Moreover, anion sensors based on Lewis acid-base interactions such as supramolecular boronate esters have also been investigated.⁸ These research activities centred on colourimetric and/or fluorometric-based sensors.⁹ Alternatively, we propose a new platform for anion sensors based on organic field effect transistors (OFETs). To date, OFET technology has been researched primarily for use in plastic-

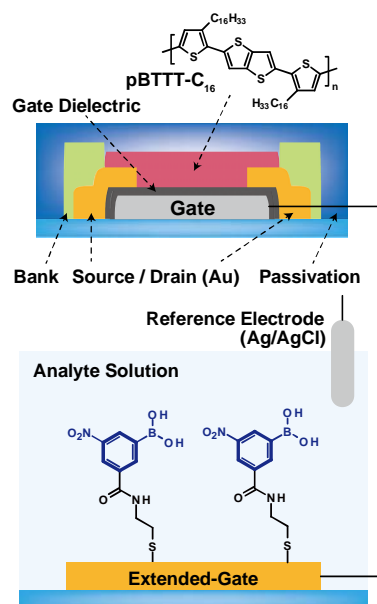


Fig. 1 Schematic structure of the anion sensor based on the extended-gate type OFET. The extended-gate electrode is functionalised with PBA.

based rollable displays,¹⁰ because of their durability, lightweight and environmentally friendly manufacturing. However, interest in OFETs and their advantages have now extended beyond information displays to sensor applications. OFETs possess attractive properties such as printability, simple integration, mechanical flexibility, and low manufacturing costs; furthermore they can be potentially applied to wearable and disposable (or recyclable) sensors. As a result, the research domain for OFET device applications has recently widened,¹¹ allowing for the novel supramolecular anion sensor platforms proposed here. As an example of anion sensors based on OFETs, we decided to employ a phenylboronic acid (PBA) derivative (which can bind basic anions) as an anion receptor,¹² and functionalise it on an OFET gate electrode. In this paper, we are the first to report an OFET sensor device modified with a supramolecular anion receptor.

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†Electronic Supplementary Information (ESI) available: General information of experiments, fabrication of the OFET device, functionalisation of the extended-gate electrode, electric characteristics of the OFET, the relationship of drain currents and threshold voltages and anion titrations. See DOI: 10.1039/b000000x. See DOI: 10.1039/x0xx00000x

For the development of anion sensor devices, we designed an extended-gate type OFET. In the designed device, a layer of gold (Au) on a thin plastic film was used as the extended-gate electrode, which allows us to functionalise its surface with the anion receptor. The device structure for the extended-gate type OFET is shown in Fig. 1. The transistor was designed to operate at low voltages¹³ in order to avoid electrolysis when immersed in water. For the active layer of the OFET, we employed a solution-processable organic semiconducting polymer poly{2,5-bis(3-hexadecylthiophene-2-yl)thieno[3,2-*b*]thiophene} (pBTTT-C₁₆).¹⁴ The fabrication details for the OFET are summarized in Supplementary Information (SI). The functionalized PBA on the gate electrode possesses a nitro group in the *m*-position to increase the Lewis acidity of boron.¹⁵ The functionalisation of the gate electrode was carried out by immersing the extended-gate electrode in a methanol solution containing 2-aminoethanethiol (AET) for preparation of a self-assembled monolayer (SAM), and then 3-carboxy-5-nitrophenylboronic acid (CNPBA) with an amide coupling reagent in DMF was dropped onto the electrode. Finally, the electrode was rinsed with DMF, ethanol and water (see the SI for details).

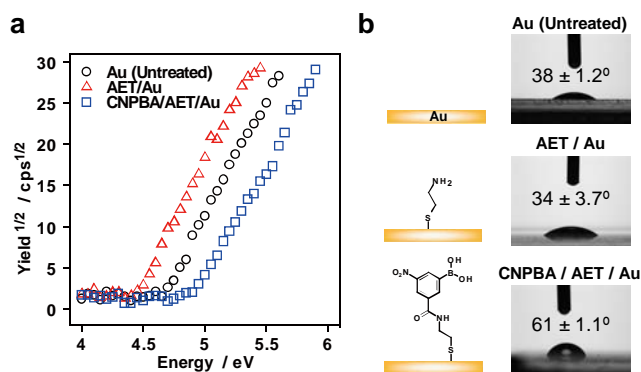


Fig. 2 (a) Photoelectron yield spectroscopy measurements of the gold gate electrode surface in air. Untreated Au (black circle), 2-aminoethanethiol (AET)-treated Au (red triangle), 3-carboxy-5-nitrophenylboronic acid (CNPBA)-treated Au (blue square). (b) Water contact angle measurements for the Au electrodes.

We first investigated whether the formation of the AET-SAM layer and the attachment of CNPBA to the Au electrode by photoelectron yield spectroscopy (PYS) in air. The results clearly showed that the work function on the AET-treated Au electrode (4.52 eV) was lower than that of the untreated Au electrode (4.66 eV) (Fig. 2a), suggesting that an electron-donating group (i.e. amino group) covered the Au surface.¹⁶ Moreover, the PYS results after immobilisation of CNPBA showed a higher work function (4.86 eV) (Fig. 2a). CNPBA is an electron-withdrawing group, and these results are in good agreement with a previous report of those of a PBA-functionalised gold film.^{11c} In addition, we measured the water contact angle on the surface of the treated Au electrodes using a contact angle goniometer (Fig. 2b). The water contact angle of the AET-treated Au electrode ($34 \pm 3.7^\circ$) was lower than that of the untreated Au electrode ($38 \pm 1.2^\circ$). In contrast, the CNPBA-treated Au electrode had a higher water contact angle of $61 \pm 1.1^\circ$. This is most likely due to the hydrophobicity of CNPBA. Additionally, X-ray photoelectron spectroscopy (XPS) revealed the presence of carbon,

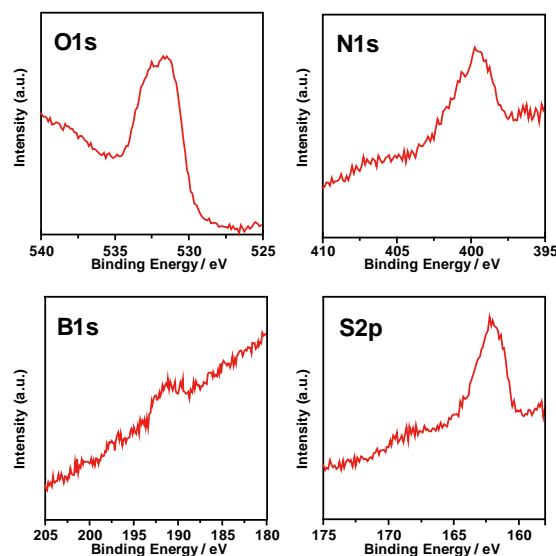


Fig. 3 XPS spectra for O1s, N1s, B1s, and S2p regions of the CNPBA-treated Au electrode.

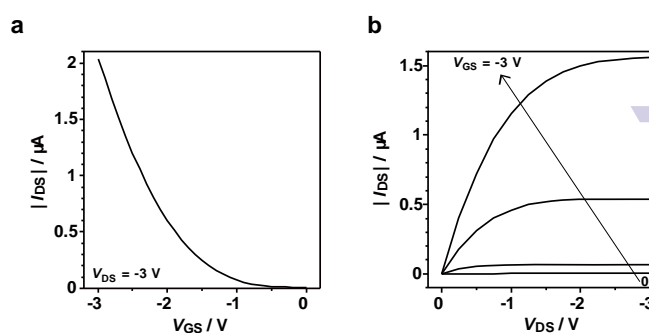


Fig. 4 Electric characteristics of the OFET (without the extended-gate) under 3 V. (a) Transfer characteristics (I_{DS} - V_{GS}) of the fabricated OFET device. (b) Output characteristics (I_{DS} - V_{DS}) of the same device.

oxygen, sulphur, and boron on the gold electrode (Fig. 3). Collectively, these characterisation results for the Au electrode confirm that functionalisation of the electrode by PBA was successfully achieved.

The electric properties of the fabricated OFET were measured by a source meter. The OFET functioned reproducibly at below 3 V (Fig. 4). By repetitive measurements, we also found that the OFET device was stable against the DC bias. (See the SI). These results mean that the device could be applied to anion sensing in water. We next examined the ability of the extended-gate type OFET to detect anions. The OFET was connected to the extended-gate electrode through a copper cable. The gate voltage was applied through a silver chloride electrode (Fig. 1). Fig. 5 shows the transfer characteristics of the OFET upon the addition of F⁻ (50 mM) in a MES (=2-(*N*-morpholino)ethanesulfonic acid) buffer solution at pH 5.5. These weak acidic conditions are important in avoiding interference of OH⁻ with PBA.¹² As a result, we observed distinct positive shifts in the transfer curves with increasing F⁻ concentrations. The limit of detection for F⁻ was estimated to be 0.7 mM.¹⁷ On the other hand, the changes in the field effect mobility and the gate-source current of the OFET devices were very small (See the SI), suggesting that

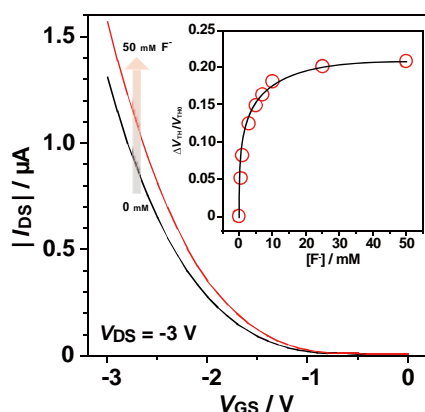


Fig. 5 Transfer characteristics (I_{DS} - V_{GS}) of the OFET device upon the addition of F^- (50 mM) in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at r.t. Inset shows the changes in threshold voltage for the OFET device by fluoride at various concentrations in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at r.t.

degradation of the OFET occurred. These observed positive shifts are attributed to changes in conductance within the OFET channel by the negatively charged anionic phenylboronate on the extended-gate electrode, such that the operating mechanism of extended-gate type FETs can be explained as an interfacial shift in potential at the gate/electrolyte interface.¹⁸

Anion selectivity was also investigated using F^- , Cl^- , Br^- , AcO^- and $H_2PO_4^-$, which represent families of biologically and environmentally important anions. Fig. 6 shows the relationship between the anion concentration and changes in threshold voltage (as calculated from the transfer characteristics) (see details of calculations in the SI). While the OFET device showed almost no responses to Cl^- and Br^- , significant responses to basic anions such as F^- , AcO^- , and $H_2PO_4^-$ were observed. The response to basic anions is attributed to the Lewis acidity of boron in PBA.^{8a} The observed selectivity and sensitivity are comparable those for PBA-based fluorescent sensors,¹⁹ colorimetric sensors²⁰ as well as electrochemical sensors²¹ that have been reported, meaning that the OFET sensor can electrically read out anion recognition behaviours of the receptors. We believe that these preliminary results are quite important because it means that OFETs can be used as a novel anion sensor platform in the same manner as fluorometric, colourimetric, and electrochemical sensors. One of the advantages of OFET-based anion sensors over these other molecular sensors is that OFETs are readily integrated into a compact device with inexpensive printed electronic circuits.²² Thus, the expertise we have gathered is expected to open avenues for the development of more practical supramolecular anion sensor devices.

In summary, we have succeeded in detecting basic anions in water using OFET-based sensor functionalised with a PBA derivative. The observed selectivity and sensitivity was derived from anion recognition ability of PBA. While we have selected a PBA derivative as a representative example of anion receptors in this research, we could similarly functionalize metal-ligand coordination and/or hydrogen-bonding based anion receptors on the gate electrode. Although these results are preliminary, we feel they validate the

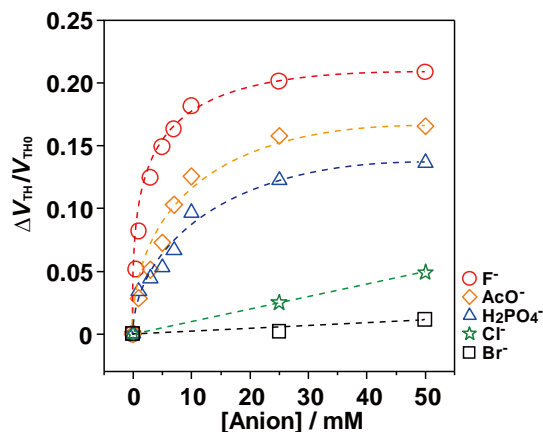


Fig. 6 Changes in threshold voltage for the OFET devices by anions at various concentrations in a MES buffer solution (100 mM) with NaCl (100 mM) at pH 5.5 at r.t. [Anion] = 0-50 mM.

potential of OFETs as a promising platform for anion sensing in supramolecular chemistry. Further development of these novel proposed OFET-based anion sensors is being carried out in our laboratory.

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