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Electrolyte gated-organic field effect transistors functionalized by lipid monolayers with tunable pH sensitivity for sensor applications

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Abstract: Electrolyte-gated organic field effect transistors (EG-OFETs) functionalized by engineered lipid monolayers (LMLs) are investigated to tune pH sensitivity for sensor application. The EG-OFET functionalized by OH-terminated LML shows linear dependence on the physiological pH range (4-8). Meanwhile, the LML with polar-head groups presents limited pH sensitivity only in a certain pH range. In contrast, the methyltrichlorosilane (MTS) passivation of the LML head-group makes the EG-OFET non sensitive in a broad pH range (1.68-12). These findings suggest that our proposed transistors have the potential to construct versatile sensor applications with the controllable pH sensitivity.

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3 In recent years, organic field effect transistors (OFETs) have been widely utilized for
4 sensor applications.¹⁻⁴⁾ OFETs provide versatile platforms to achieve high selectivity and
5 sensitivity even with small input signals.⁵⁻⁹⁾ With respect to sensor applications in the
6 aqueous environment, liquid electrolytes have been widely used as electrical gates in these
7 transistors.¹⁰⁻¹⁵⁾ Then, metallic gate electrode is immersed into the electrolyte solution. Of
8 importance is that the electrolyte-gated OFETs (EG-OFETs) effectively work at the
9 millivolt range. This is owing to the high capacitance ($1-20 \mu\text{Fcm}^{-2}$)^{16,17)} of an electrical
10 double layer (EDL) formed at the interface between the electrolyte solution and organic
11 semiconductor channel. This merit leads to an ultra-low threshold voltage (V_{th}) under 1 V,
12 which is effective to avoid any electrochemical reaction in the electrolyte solution.^{17,18)}
13 Here, it should be noted that V_{th} is highly responsive to surface charges provided from
14 analytes such as ions or biomolecules.^{8,12,19)} Therefore, the ultra-low V_{th} is advantageous to
15 detect even small signals.
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17 Because of these features, the EG-OFETs are suitable for sensing ions and biomolecules
18 in the aqueous environment. However, the EG-OFET-based sensors faced following
19 obstacles. First, the detection of these analytes is typically carried out in the presence of
20 interfering ions, e.g., potassium and sodium. These ions are well known to degrade the
21 transistor performance because they act as electrical dopants for OFETs.^{16,17,19)} The stable
22 operation of EG-OFETs in such aqueous environment, therefore, still remains as a
23 challenge.^{17,20-22)} Second, specific sensing probes should be attached on the surface of the
24 transistor channels for detecting analytes such as ions and proteins.
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26 To satisfy these requirements, we investigated the EG-OFETs with engineered lipid
27 membranes. The ultrathin lipid monolayers (LMLs) with the thickness of 2.2 nm ²³⁾ were
28 formed on the poly(3-hexylthiophene-2,5-diyl) (P3HT) films, which were employed as
29 semiconductor channels due to its stability in the aqueous environment.^{10,15)} The first
30 striking point is that the LMLs was proved to protect the transistor channels from direct
31 exposure to the electrolyte solution. That is, LML enabled the stable transistor operation
32 even in aqueous conditions by reducing electrochemical doping into the transistor channels.
33 Second, the LMLs were functionalized by attaching head groups to provide capability for
34 tuning pH sensitivity. Then, stability, repeatability and sensitivity to pH levels of the
35 EG-OFETs were examined by changing head-groups of the LMLs. Importantly, we found
36 that the transistors with OH-terminated LMLs demonstrated a linear sensitivity with pH
37 level in the range of 4 to 12. Meanwhile, methyltrichlorosilane (MTS)-terminated LMLs
38 showed no sensitivity against pH levels and significantly stable operation even with the
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3 presence of high ion concentration in the electrolyte solution. In this manner, our
4 EG-OFETs with engineered LMLs provide an innovative concept for further biosensors or
5 chemical sensors.
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8 Figure 1 (a) shows the structure of the EG-OFET, molecular structure of P3HT and
9 those of LMLs. Of importance is that the LMLs have distinct head groups. The first LML
10 consists of phosphocholine (DCPC) lipids. This lipid has a zwitterion with a large
11 permanent dipole moment induced by a negative charge of phosphate (PO_4^-) and a positive
12 charge of trimethylamine ($\text{N}^+(\text{CH}_3)_3$) at the head group. The second one is DC-glycerol
13 (DCOH) lipid monolayer, which has the neutrally charged OH-functional groups. Then, the
14 OH-functional groups can be further functionalized by MTS groups to form the third LML
15 (DC-MTS).
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22 The top-gate and the bottom-contact-type EG-OFETs were prepared on 200-nm-thick
23 $\text{SiO}_2/\text{p-Si}$ substrates, where P3HT films were used as the transistor channel. First, source
24 and drain electrodes were patterned on $\text{SiO}_2/\text{p-Si}$ substrates through a shadow mask by
25 thermal evaporation. P3HT powder (Sigma Aldrich) was dissolved in chlorobenzene
26 solvent, followed by heating the solution at 60 °C for 30 minutes to obtain 0.75 wt%
27 solution. After passing through a filter with a pore size of 200 nm, P3HT solutions were
28 spin-coated on the substrates with patterned electrodes. The P3HT films thus prepared
29 were annealed at 150 °C in a vacuum to eliminate the residual solvent. Finally, a PDMS
30 (polydimethylsiloxane) container was carefully sealed on top of the P3HT film. The gate
31 bias voltage was applied by the immersion of an Au gate electrode in electrolyte solution.
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39 Lipid molecules formed a monolayer on the P3HT film by following protocol.^{15,23,24)}
40 1,2-bis(10,12-tricosadiynoyl)-sn-glycero-3-phosphocholine phospholipid (DCPC) in the
41 form of powder was purchased from Avanti Polar Lipids (AL, USA) and used as received.
42 DC-glycerol (DCOH) lipids were synthesized from DCPC lipid (Fig. S1).^{8,23,25)} A LML of
43 DC-glycerol was formed on the P3HT film based on the hydrophobic interaction between
44 alkyl chains of the DCOH lipid and P3HT film. The polymerization at the middle of lipid
45 molecules (Fig. S2) improved the mechanical and electrical stability of LML.^{23,24)} Then,
46 DC-MTS were obtained by exposing the device to the MTS solution diluted by
47 1,4-dioxane (Sigma-Aldrich). The more detailed conditions were described in the
48 supporting information.^{8,23)} Consequently, the ultrathin (2.2 nm) phospholipid monolayer
49 sustainably covered the P3HT surface. The attenuated total reflection Fourier transform
50 infrared (ATR-FTIR) measurement confirmed the formation of the LML on P3HT film.²⁴⁾
51 The surface morphology of pristine P3HT and lipid on P3HT were examined by AFM (SII,
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3 SPI4000). AFM images showed the flat P3HT film surface without (Fig. 1(b)) and with
4 (Fig. 1(c)) the DCPC. The surface roughness (RMS) values were 0.56 nm and 0.92 nm,
5 respectively. P3HT films with DCOH and DC-MTS also showed similar results with RMS
6 values of 0.85 nm and 0.77 nm, respectively, proving that the uniform formation of the
7 LMLs on the P3HT film.
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11 First of all, we investigated fundamental properties of three kinds of EG-OFETs: the
12 pristine P3HT without LMLs and the P3HT with respective LMLs (DCPC and DCOH).
13 The I-V curves were measured by using a semiconductor parameter analyzer (Agilent
14 B1500A) under ambient conditions. The phosphate-buffered solution with a fixed pH of
15 6.86 was used as an electrolyte gate to evaluate the performance of EG-OFET. Figure 2
16 shows the drain current (I_{DS})-gate voltage (V_{GS}) curves of three devices, where the gate
17 voltage was swept from +0.4 V to -0.5 V at a fixed drain voltage of -0.5 V. The saturation
18 region was clearly observed in a typical output curve of EG-OFET in Fig. S3. The V_{th} was
19 calculated with the following equations.²⁶⁾
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$$I_{DS} = \frac{W}{2L} \mu C_i (V_{GS} - V_{th})^2 \quad (1)$$

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32 where W (100 μm), L (2000 μm), μ and C_i are the width and length of the transistor
33 channel, carrier mobility and the capacitance of the gate dielectric layer, respectively. The
34 V_{th} of the pristine P3HT transistor was estimated to be +70 mV (± 27 mV). Meanwhile,
35 those of the transistors with DCOH and DCPC LMLs were -29 mV (± 33 mV) and +24
36 mV (± 34 mV), respectively. In this manner, three devices showed the ultralow threshold
37 voltage (V_{th}), even though there were slight differences in the V_{th} values. Additionally, the
38 estimated carrier mobilities of pristine P3HT and P3HT with DCOH lipid were same order,
39 $7.2 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $4.3 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively. The mobilities are comparable to
40 those reported in the P3HT-based EG-OFETs,^{10,17)} suggesting that the LMLs had moderate
41 impact on the carrier transport in the channel layers.
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51 Clear differences were observed in the forwards and backwards potential sweeps. The
52 pristine P3HT showed a hysteresis around low gate bias range of +0.4 to 0 V (Fig. 2(a)). In
53 contrast, the EG-OFETs covered by the LMLs demonstrated negligible hysteresis in the
54 loops as can be seen in Figs. 2(b) and (c). The observed hysteresis in the pristine P3HT can
55 be ascribed to the ion doping from the electrolyte solution into the P3HT channel during
56 the potential sweeps. Meanwhile, the LMLs suppressed such electrochemical doping effect.
57 This advantage of the LML was pronounced in the long-term operation as described below.
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3 The long-term operation stability in the electrolyte solution is strictly required for
4 sensor applications. The operation stability of three devices was evaluated by repeating
5 measurements ten cycles for 2 hours in electrolyte solution. We observed the gradual
6 decrease in V_{th} with significant deviation in the pristine P3HT EG-OFET as shown in Fig.
7 2(d). This result can be explained by the doping from electrolyte solution into the P3HT
8 channel. In contrast, both LMLs on the P3HT films improved the stability of the EG-OFET
9 for long-term measurement; no shifts in V_{th} were observed as shown in Figs. 2(e) and 2(f).
10 The deviations at each cycle were also negligibly small. These results also indicate that the
11 LML is effective to reduce the ion doping into the P3HT channel. This is a clear advantage
12 for the sustainable operation of EG-OFETs in electrolyte solution.
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20 For sensor application, including specific ion and biological sensors, the control of pH
21 sensitivity is a key factor. Therefore, we discussed how to design the head groups of LMLs
22 for tuning pH sensitivity. The pH sensitivities of EG-OFETs with two kinds of LMLs,
23 DCOH and DCPC, were compared to examine the capability of EG-OFETs with LMLs as
24 pH sensors. Then, the pristine EG-OFET with a non-functionalized P3HT channel was
25 evaluated as a reference. The standard pH solutions in a range from 1.68 to 12 were used to
26 examine the pH sensitivity of devices. The variation in the V_{th} (ΔV_{th}) depending on the pH
27 level was measured for respective EG-OFETs. The transfer curves were recorded in the
28 V_{GS} range of 0 to -300 mV at fixed V_{DS} of -300 mV. The low range of V_{GS} was to avoid
29 any electrolysis process caused by pH variation.¹⁸⁾ The obtained results showed significant
30 differences in ΔV_{th} as shown in Figs. 3(a)-(c). The pristine EG-OFET showed no
31 dependence of V_{th} on the pH level (Figure 3(a)). This was resulted by the non-pH
32 sensitivity of alkyl chains of the P3HT film. However, the pristine EG-OFET presented
33 significant deviations of V_{th} . The doping of electrolyte ions is the reason for the unstable
34 operation of the pristine EG-OFET in pH (electrolyte) solution.
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46 In a case of the DCPC LML, no clear dependence of ΔV_{th} was observed although it
47 showed wide variations against pH levels as shown in Figure 3(b). This result was
48 probably due to the intrinsic characteristics of zwitterionic head groups of DCPC lipid.²⁷⁻
49 ³²⁾ In pH range of 4 to 8.5, the DCPC lipid is electrically neutral due to the co-existence of
50 both positive and negative charged groups.^{28,29)} As a result, the transistor with DCPC lipid
51 showed only marginal ΔV_{th} in this pH range. Meanwhile, the V_{th} was dramatically shifted to
52 positive side above pH level of 8. This is due to the neutralization of positively charged
53 groups ($pK_{a2} \approx 10$) while the negatively charged groups still remained.^{31,33,34)} The negative
54 ΔV_{th} observed below pH of 4 was supposed to be induced by positively charged head
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3 groups ($\text{pK}_{a1} \approx 1.7$). In this manner, DCPC LML showed complicated variations in ΔV_{th}
4 depending on the surface charges.
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6 In contrast, the DCOH LML obviously showed linear dependence of ΔV_{th} on the pH
7 level as shown in Figure 3(c). The ΔV_{th} was ranging from +50 mV to -100 mV in the range
8 of pH from 4 to 12. The sensitivity is approximately 17.76 mV per pH. This result is
9 explained by the interaction of H_3O^+ at OH group. This formation caused the variation in
10 the charge density on the surface^{35,36}, modulating the capacitance of EDL³⁶. As a result,
11 the charge accumulation in the transistor channel was modulated. Hence, the transfer
12 curves gradually shifted to negative gate voltage according to the pH level. This tendency
13 is shown in Fig. S6. Additionally, the devices showed the chemically stability with small
14 hysteresis when changing pH values from acid to and vice versa (Fig. S7). Under pH of 4,
15 the ΔV_{th} showed the independence on the pH level. These results emphasize the importance
16 of head groups of the LML. The chemical reactions of the head groups in different pH
17 levels significantly affect on the performance of the EG-OFETs. Furthermore, the
18 EG-OFET with the DCOH showed a linear sensitivity with the physiological pH range of
19 4-8, which is adaptable in biology and medicine applications.³⁷ This finding is useful to
20 fulfill sensing applications with biological friendliness.
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32 However, the development of sensors with non-sensitivity to pH variations is also
33 crucial in some cases. This is because the sensors are required to selectively detect only the
34 analytes (ions or proteins) even in electrolyte solution with different pH levels.⁸ For these
35 purposes, we modified the DCOH LML by silanization to convert the head group from OH
36 to MTS (denoted as DC-MTS LML). Then, we evaluated the pH sensitivity and operation
37 stability of the EG-OFET with DC-MTS LML. Details of the measurement conditions
38 were same to those of other EG-OFETs. The low V_{th} (+120 mV) was confirmed.
39 Importantly, the transistors became non-sensitive to the pH variation as shown in Fig. 4(a).
40 No variation in V_{th} ($\Delta V_{\text{th}} = 0$ mV) was observed regardless of pH levels. The deviation of
41 V_{th} at each pH level was also enough small due to the reduced doping effect into the P3HT
42 film. The results indicate that the MTS groups successful passivated the OH-groups.
43 Furthermore, the devices showed a stable operation even after exposing to the organic
44 solvent (Fig. 4(b)). The V_{th} showed a negligible change even after repeated measurements
45 for 2 hours. It should be emphasized that this technique provides the potential benefit for
46 passivating OH terminals as well as for grafting other receptors onto the LML at
47 R-positions in Fig. S2. That is, the EG-OFET with DCOH monolayer has high potential in
48 further functionalization by specific probes for versatile sensor application.
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3 In summary, we have developed novel EG-OFETs by functionalizing transistor channels
4 with the engineered LMLs. The engineered LML contributed to improve EG-OFET
5 operation by preventing the doping effect from electrolyte solution into the transistor
6 channels. The ΔV_{th} was negligible small even after repeated operations in the electrolyte
7 solution for a long time. The performance of EG-OFET was found to be controlled by the
8 different functional groups of the LML. The EG-OFET with DCOH LML showed the pH
9 sensitivity which satisfied the physiological pH range (4-8) as reported by G. K.
10 Schwalfenberg et al.,³⁷⁾ On the contrary, the EG-OFET the DC-MTS LML showed the
11 independence on pH level in a large range (1.68 to 12). This result implies that the
12 EG-OFET with DCOH LML has a potential for further sensor development because
13 specific receptors can be easily attached to LML for the detection of ions and protein
14 molecules. Our approach will pave the way for development of new sensor applications in
15 chemical and biological fields.
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Template for APEX (Jan. 2014)

Figure Captions

Fig. 1. (a) A schematic illustration of electrolyte gated-organic field transistor with three kinds of LMLs. The molecular structures of respective lipids, i) DCPC, ii) DCOH and iii) DC-MTS, are shown on the right side. The surface morphology of (b) pristine P3HT film and (c) DCPC lipid monolayer on the P3HT film. The AFM images showed the uniform of P3HT film before and after lipid monolayer deposition.

Fig. 2. Transfer curves of EG-OFETs with (a) pristine P3HT, (b) P3HT with DCPC layer and (c) P3HT with DCOH layer. The variations in V_{th} (ΔV_{th}) with repeated transistor measurements: (d) pristine P3HT (e) P3HT with DCPC LML (f) P3HT with DCOH LML.

Fig. 3. Variation in threshold voltage (ΔV_{th}) of EG-OFET in electrolyte solutions with different pH levels: (a) pristine P3HT (b) P3HT with DCPC lipid and (c) P3HT with DCOH lipid.

Fig. 4. (a) pH dependence of ΔV_{th} , showing no variations. (b) ΔV_{th} after repeated operations.

Template for APEX (Jan. 2014)

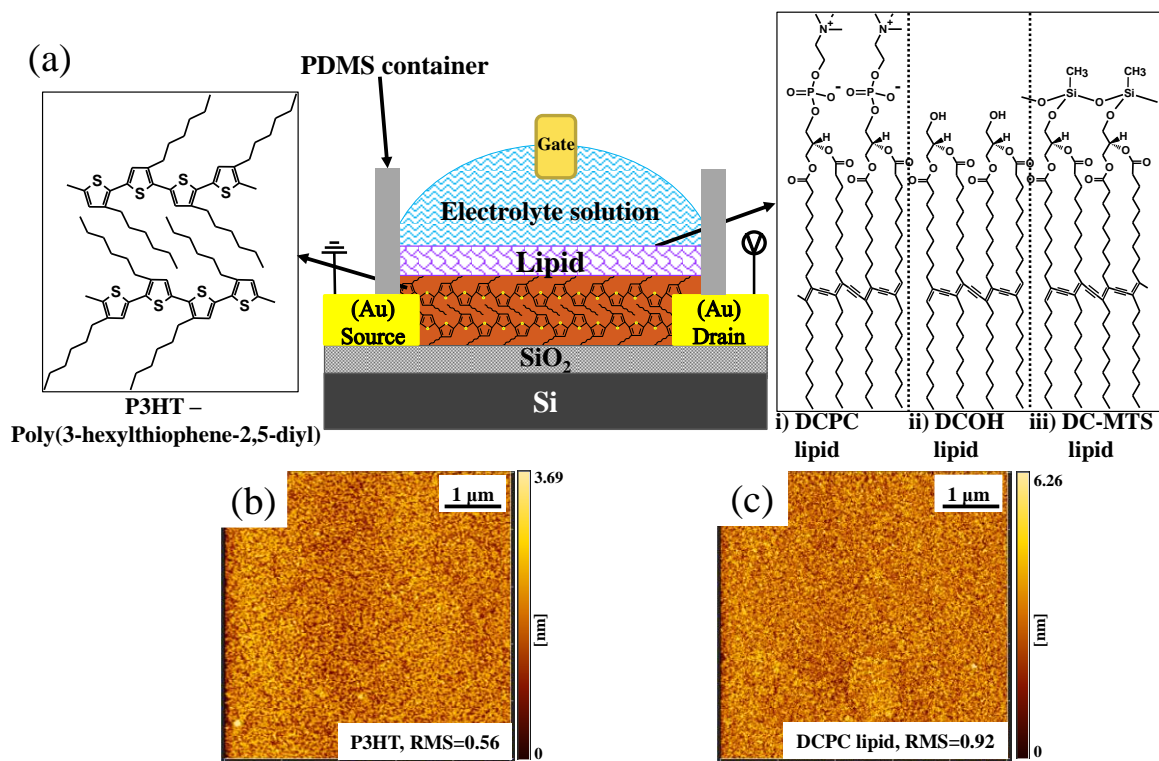


Fig.1.

Template for APEX (Jan. 2014)

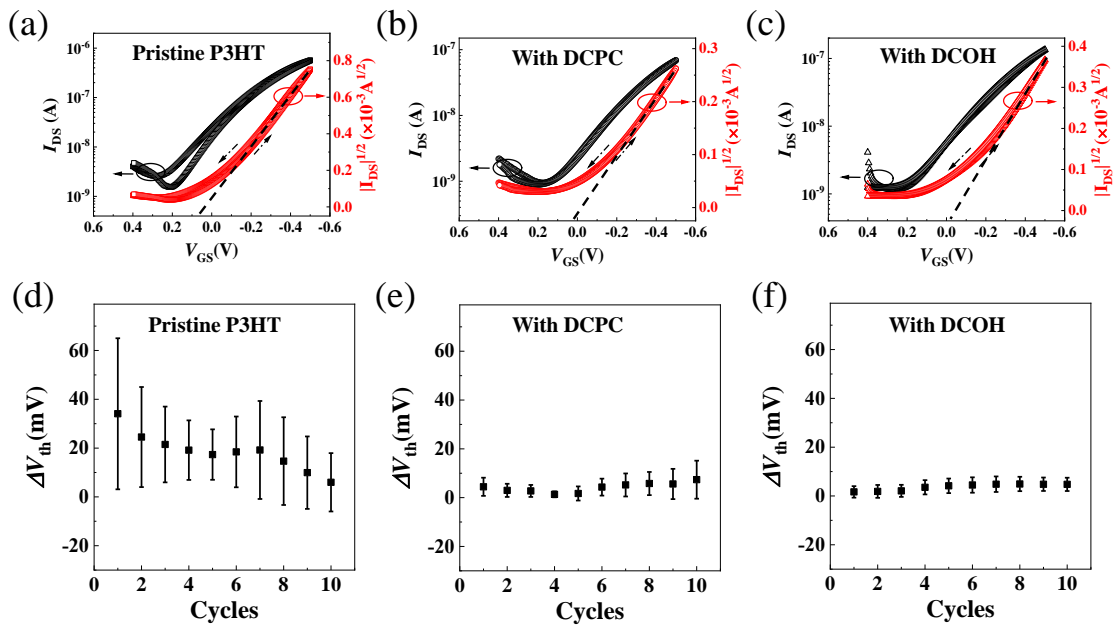


Fig. 2.

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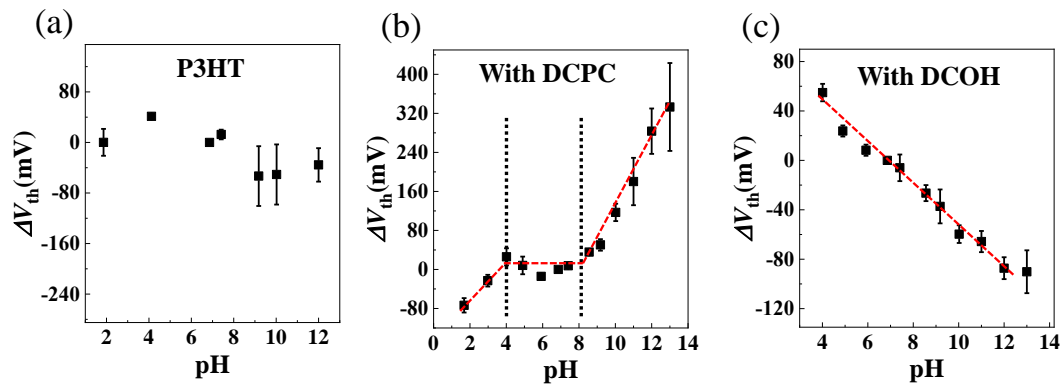


Fig. 3.

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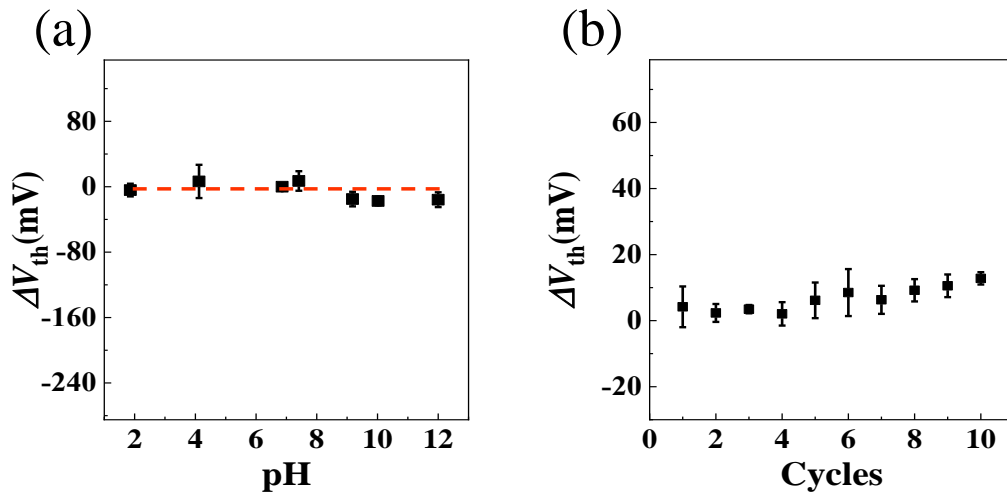


Fig. 4.