Supporting Information

Double Input Capacitively Coupled Contactless Conductivity Detector with Phase Shift

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This document provides extra information concerning the experimental procedure described in the manuscript, including the structures of three-way DIC^4D (Figure S-1); Exploration of DIC^4D with spectrum analyzer (Figure S-2); Block diagram of the other double input capacitively coupled contactless conductivity detector (Figure S-3); Responses of DIC^4D at different frequencies (Figure S-4); Wave interfere results of different wave forms (Figure S-5); Responses of DIC^4D and C^4D with different inputs and different concentration of KCl solutions (Figure S-6); Responses of C^4D and three-way DIC^4D with a blocked branch after normalization (Figure S-7); Response curves of C^4D and the three-way DIC^4D (Figure S-8); Responses of 15 different solutions (Figure S-9); Response reproducibility of DIC^4D (Figure S-10).

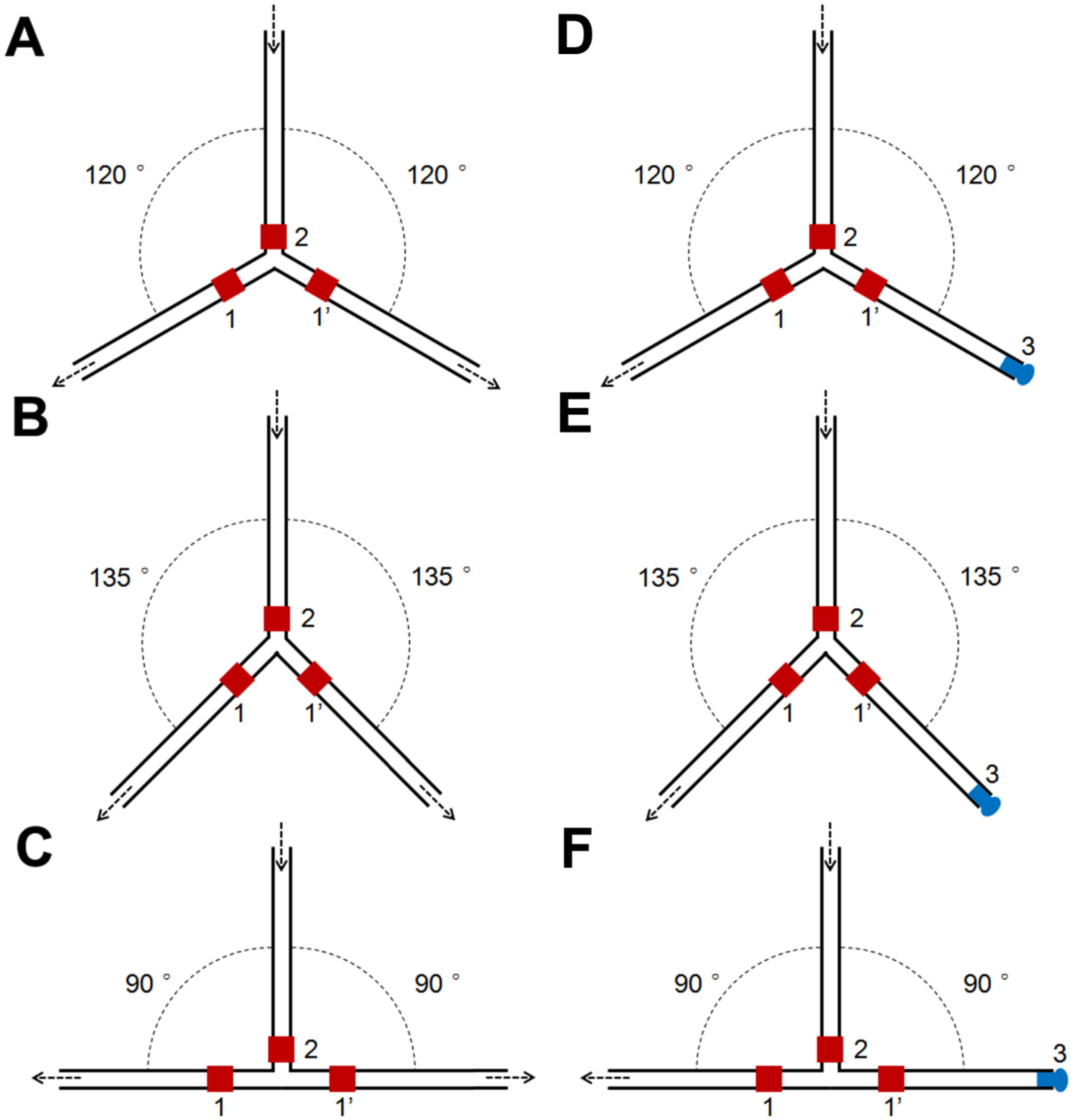

Figure S-1. Structures of three-way DIC^{4}D. (A) Electrode with three angles of 120°, 120°, and 120°, one input port, two output ports. (B) Electrode with three angles of 90°, 135°, and 135°, one input port, two output ports. (C) Electrode with three angles of 90°, 90°, and 180°, one input port, two output ports. (D) Electrode with three angles of 120°, 120°, and 120°, one input port, one output port. (E) Electrode with three angles of 90°, 135°, and 135°, one input port, one output port.

(F) Electrode with three angles of 90°, 90°, and 180°, one input port, one output port.

The outer diameter of the three-way DIC^4D is 3 mm, and the inner diameter is 1.5 mm. The three angles of the detector are 90°, 90°, and 180°; 90°, 135°, and 135°; 120°, 120°, and 120°, respectively. The detector had also been studied in two approaches. One approach is that one branch of the detector is the input port, and two other branches are the output ports. The other approach is that one branch is blocked and filled with distilled water or air, one branch is the input port while the other branch is the output port.

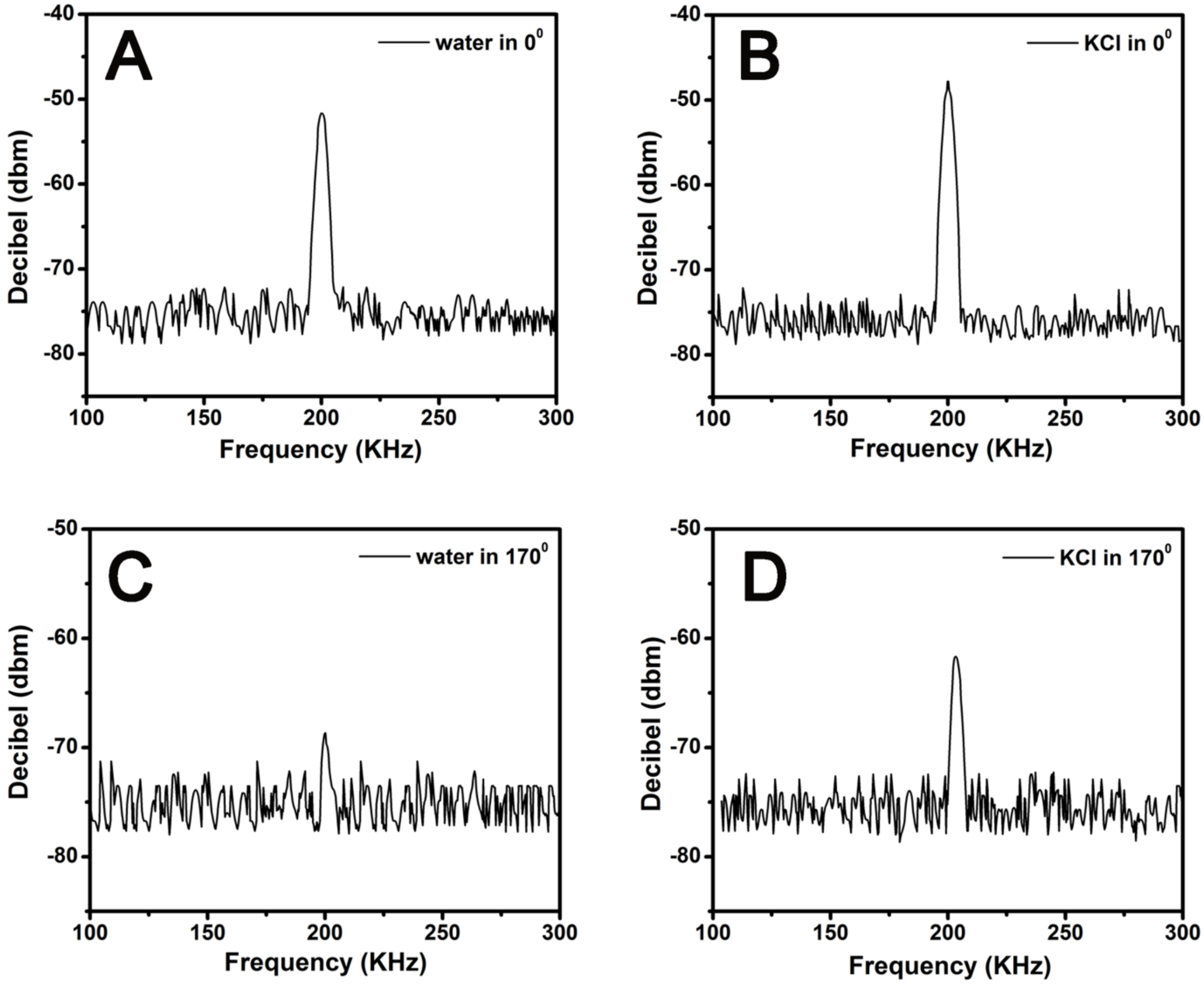

Figure S-2. Exploration of DIC^4D with spectrum analyzer. The x-axis represents the frequency, the y-axis represents the decibel. (A) Water measured at 0°. (B) KCl solution measured at 0°. (C) Water measured at 170°. (D) KCl solution measured at 170°. All the other conditions are all the same.

A spectrum analyzer was employed to analysis the response difference between C^4D and DIC^4D. 5 mM KCl solution was used as a sample solution, the frequency was 200 kHz, the length of the electrode was 5 mm, the length of the gap was 2 mm, and distilled water was used as background electrolyte. The ratio of the response of KCl solution to water was 1.55 at the phase difference of 0°. The ratio of the response of KCl solution to water was 1.80 at the phase difference of 170°.

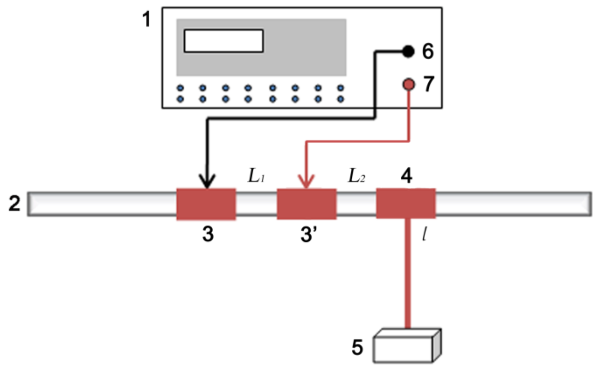

Figure S-3. Block diagram of the other double input capacitively coupled contactless conductivity detector. (1) Function generator with two channels. (2) Glass tube used for detection. (3) Input electrode 3 and electrode 3'. (4) Output electrode. (5) Data acquisition system. (6) Channel 1 of the function generator. (7) Channel 2 of the function generator. L_1 and L_2 are the length of the gap.

The input electrodes 3 and 3' were placed at one end while the output electrode 4 was placed at another end. In this asymmetric device, the signals firstly interfered with each other at input electrode 3' when they transmitted through the solution. Lengths of the solution were L_1+L_2+l and L_2 respectively.

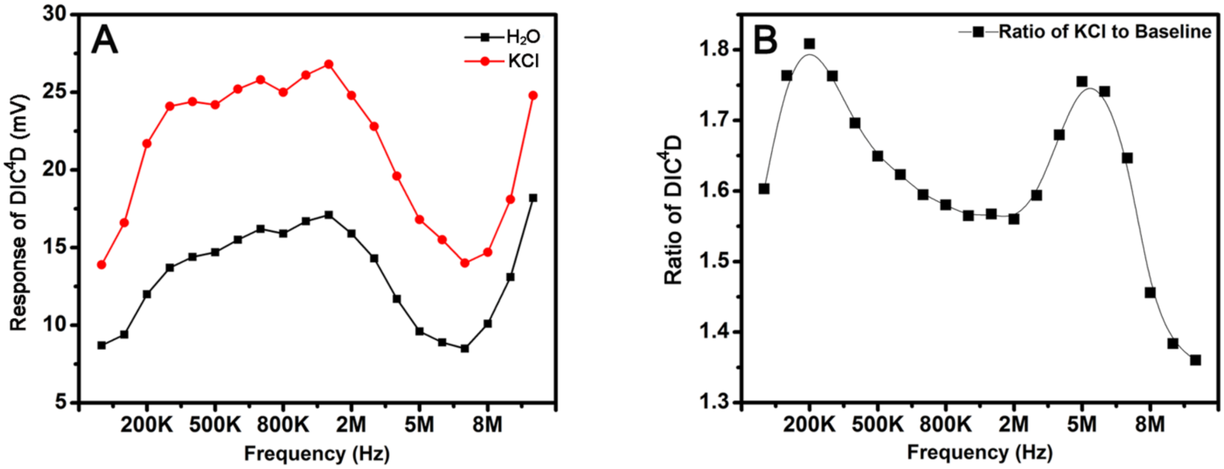

Figure S-4. Responses of DIC^4D at different frequencies. (A) Response of distilled water and 5 mM KCl at frequency ranges from 50 kHz to 10 MHz. (B) Ratio of the response at the same frequency range. Ratio at 200 kHz is the highest, and after 10 MHz, the response is even higher while the ratio is getting closer to 1.

Impedance of the electrode capacitor and solution capacitor were reduced when the working frequency increased from 50 kHz to 10 MHz. In the process of detection, the phase difference between the two input signals was set to 170°. The ratio was the highest when the frequency was 200 kHz. When the frequency was higher than 5 MHz, the signal measured was higher but the ratio became smaller. When the frequency was higher than 10 MHz, the ratio was the lowest.

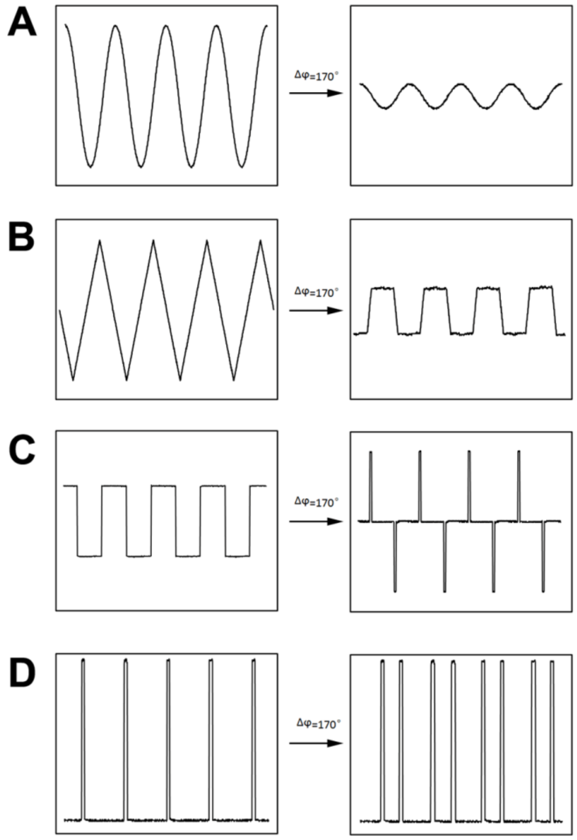

Figure S-5. Wave interfere results of different wave forms. The phase angel is set to 170°. (A) The response of the sine wave interferes with another sine wave at 170°. (B) The response of the triangle wave interferes with another one at 170°. (C) The response of the square wave interferes with another one at 170°. (D) The response of the pulse interferes with another one at 170°. (E) The response of the interference of four different wave forms measured with spectrum analyzer.

Four different wave forms were studied in detail with oscilloscope and signal generator. Two same signals interfere with each other at 170°. Signal strength of the output sine wave was the weakest. Strength of the output triangle wave was stronger than that of the sine wave. Strength of the square wave was the highest. The pulse is kept constant after signals interfere with each other, and the ratio of the pulse is the lowest.

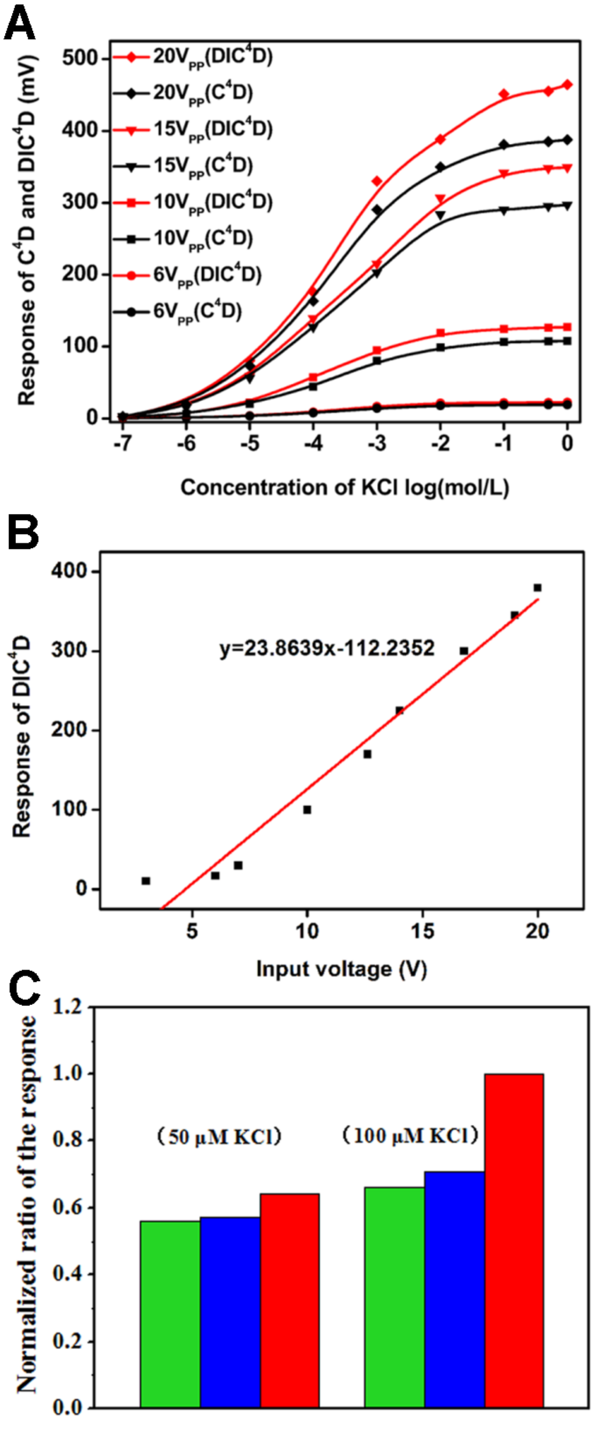

Figure S-6. Responses of DIC^{4}D with different inputs. (A) Responses of DIC^{4}D and C^{4}D with different inputs and different concentrations of KCl solution. 6 V_{PP}, 10 V_{PP}, 15 V_{PP}, and 20 V_{PP} are applied respectively. (B) Responses of DIC^{4}D with different inputs. Input voltages from 3 V_{PP} to 20

V_{PP} are used respectively. The concentration of KCl solution is 5 mM. (C) Normalized ratio of the response of C^4D and DIC^4D at different phase angles. The concentrations of KCl solution were 50 μM and 100 μM. The green bar graph represents the DIC^4D mode with two input applied voltages of 6 V and phase angle of 0°, the blue bar graph represents the C^4D mode with input applied voltage of 12 V, the red bar graph represents the DIC^4D mode with two input applied voltages of 6 V and the phase angle of 170°.

Two signal generators were employed because two channels of one signal generator can not provide 20 V_{PP} at the same time. Input voltages from 3 V_{PP} to 20 V_{PP} were used. Figure S-6A shows the response of DIC^4D and C^4D with different inputs. Figure S-6B shows that when the input increases, the sensitivity improves, that explains why higher inputs improve the sensitivity in those literatures. As a contrast, Figure S-6C shows that when the voltage of 6 V is applied simultaneously to the two input electrodes for the DIC^4D mode, it is obvious that when the phase is set to 0°, the sensitivity is a little lower than that of the traditional C^4D with input applied voltage of 12 V. However, when the phase is set to 170°, the sensitivity is obviously increased. The results indicate that the response of the DIC^4D mode is substantially higher than that of C^4D mode.

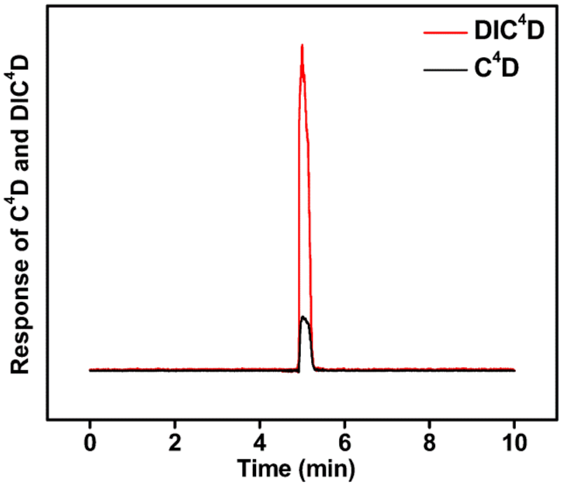

Figure S-7. Responses of C^{4}D and three-way DIC^{4}D with a blocked branch after normalization.

Responses of C^{4}D and three-way DIC^{4}D with angles 120°, 120°, and 120° in flow injection was shown in Figure S-7. One branch of the three-way DIC^{4}D is blocked, and filled with air. When one branch is blocked and filled with air, another branch is filled with KCl solution, the input signals are completely different. The output signal is very small when distilled water is running. As KCl solution is running, the output signal is received by the signal from the electrode filled with KCl solution minus that from the electrode filled with air. It is obvious that the ratio is highly increased.

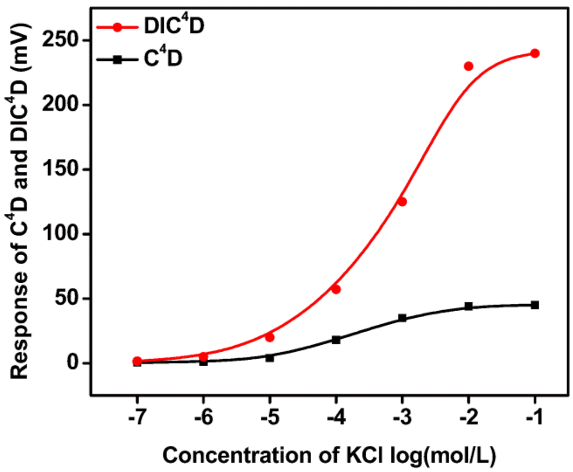

Figure S-8. Response curves of C^4D and the three-way DIC^4D. Response of the concentration of KCl solution ranges from 10^{-7} M to 10^{-1} M of the three-way DIC^4D.

The responses of different concentrations of KCl solution were studied. C^4D and three-way DIC^4D with a blocked branch filled were employed. The slope of the three-way DIC^4D is 69.78 while that of C^4D is 13.70. The sensitivity of the three-way DIC^4D was significantly improved. In DIC^4D, the baseline is largely decreased while the peak is nearly the same, thus highly increasing the ratio. The blocked branch with water was also studied, the performance is worse than that filled with air for the water would be contaminated when the KCl solution is running.

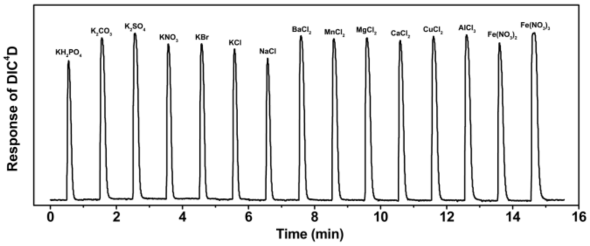

Figure S-9. The responses of 15 different solutions (Concentration: 1mM). Sample: (1) KH_2PO_4, (2) K_2CO_3, (3) K_2SO_4, (4) KNO_3, (5) KBr, (6) KCl, (7) NaCl, (8) $BaCl_2$, (9) $MnCl_2$, (10) $MgCl_2$, (11) $CaCl_2$, (12) $CuCl_2$, (13) $AlCl_3$, (14) $Fe(NO_3)_2$, (15) $Fe(NO_3)_3$.

The concentration of 15 different solutions was 0.001 M. It is obvious that the response of KH_2PO_4 solution was the lowest, and the responses of $BaCl_2$ and $Fe(NO_3)_3$ solutions were the highest. It is because the electrical conductivity of KH_2PO_4 solution is the lowest and that of $BaCl_2$ and $Fe(NO_3)_3$ solutions are the highest.

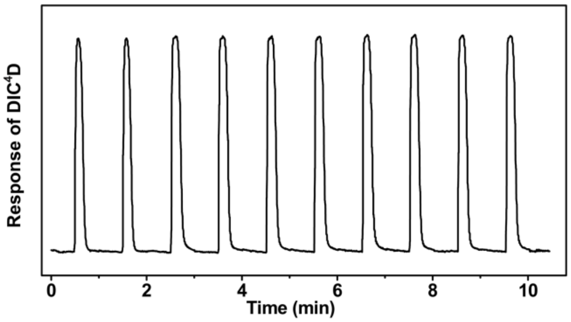

Figure S-10. The response reproducibility of DIC^{4}D. 5 mM KCl solution was measured 10 times with DIC^{4}D in the capillary. The relative standard deviation was 0.7%.

5 mM KCl solution was used to evaluate the reproducibility of DIC^{4}D. It was carried out 10 times with the capillary in flow injection device. The relative standard deviation of the responses of KCl solution was 0.7%. A good reproducibility of DIC^{4}D is obtained.