Supplementary Information

Quantum Dot–Based Molecularly Imprinted Polymers on Three-Dimensional Origami Paper Microfluidic Chip for Fluorescence Detection of Phycocyanin

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Experimental details

The comparison of fluorescence intensity. The 3 ml 5×10^{-3}M QDs solution was added and made a covalently immobilization on the paper through EDC/NHS reaction by using 3 ml 20 mg/mL EDC and 3 ml 10 mg/mL NHS, oscillating at 100 rpm for 4 hours. The comparative experiment let 3ml 5×10^{-3}M QDs physically adsorbed on the paper by adding 6 ml water as a control to take place of EDC and NHS, oscillating at 100 rpm for 4 hours. Then we tested the fluorescence intensities of QDs on paper (covalently immobilized or physically adsorbed) before and after rinsing.

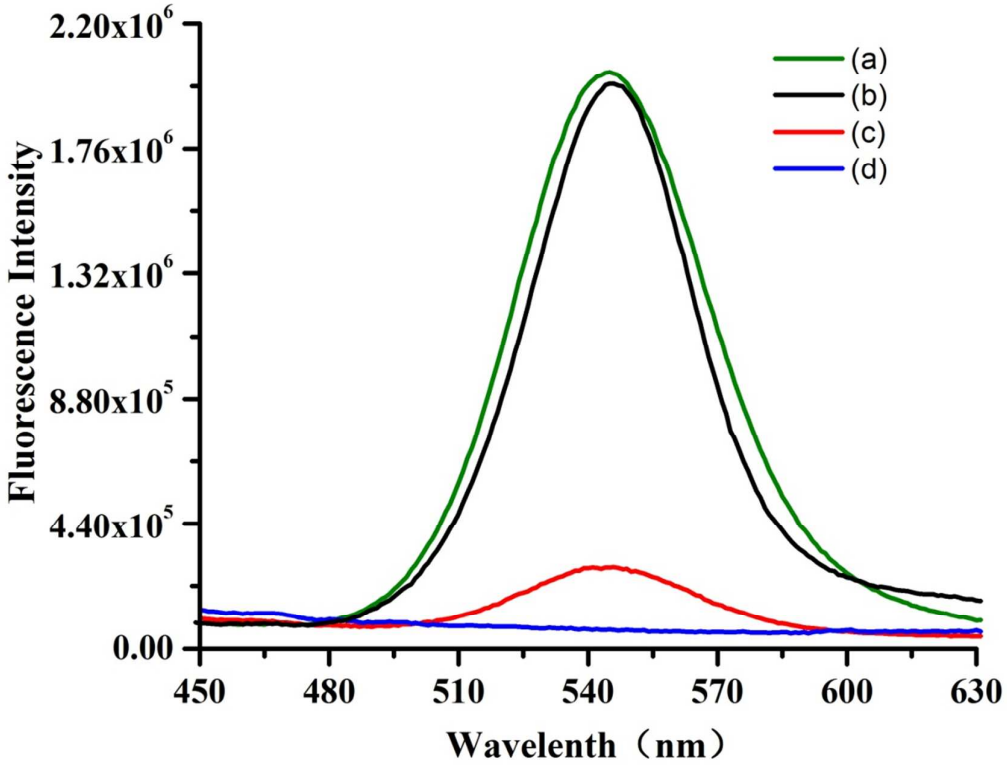


Fig S1. The comparison of fluorescence intensity. The fluorescence intensities before rinsing (a) paper@QDs (c) physically adsorbed QDs. And rinsing the chips three times by DI water, we tested the fluorescence intensity of (b) paper@QDs (d) physically adsorbed QDs

As displayed in Fig. S2, the Si-O stretching vibration could be ascribed to the characteristic peak around 466 and 786 cm^{-1} and the wide and strong absorption band around 1060 cm^{-1} could be attributed to stretching vibrations of Si−O−Si. Furthermore, the filter paper fiber contained some silica ingredients, which in a subsequent synthesis of molecularly imprinted join TEOS led to silica vibration peak strengthening. The stretching vibration of N−H at 1631 and 3432 cm^{-1} proved that a large number of amino groups were modified onto the surface of paper. The data show 1427 cm^{-1} vibration absorption peak corresponding to the formation of carboxyl and amino groups by amide bond, and, at the same time, an absorption peak in the 1548 cm^{-1}, which could be assigned to the vibration of the quantum dots absorption peak. The characteristics of the silica peak confirm successful CdTe quantum dots grafting. The vibration absorption peak of quantum dots was reduced and the Si-O characteristic peak increased, which proved that the PC imprinted polymer successfully grafted on the surface of quantum dots. Figure S2 shows the ultraviolet absorption of 0.25 mg/mL phycocyanin spiked with 40 μL APTES. The ultraviolet absorption peak of phycocyanin at 600 nm was obviously reduced, proving that the functional monomer had good combination.

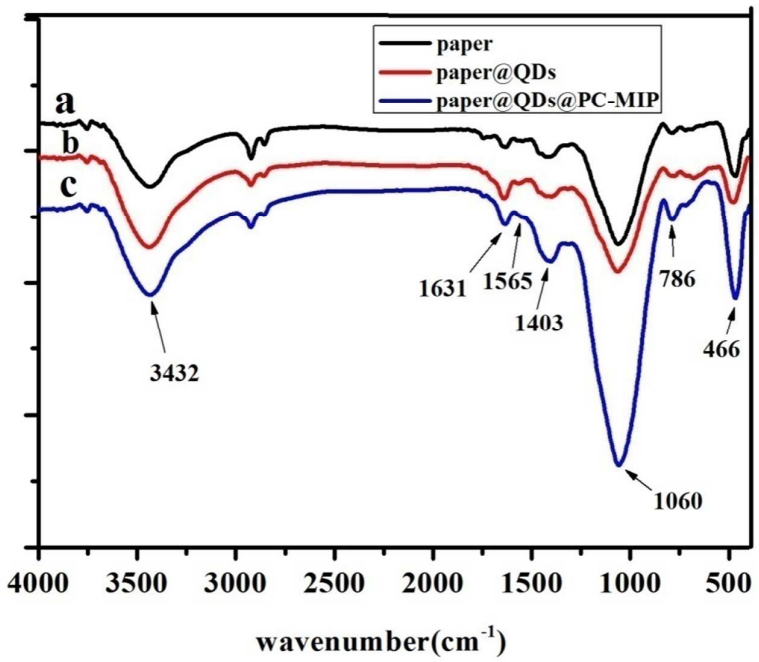
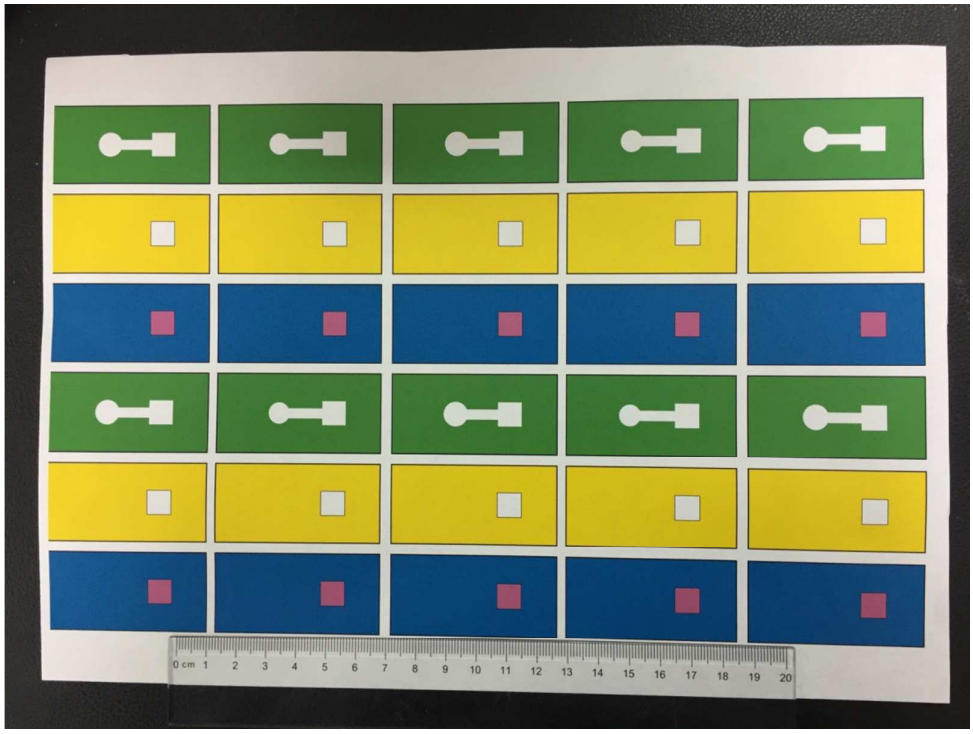
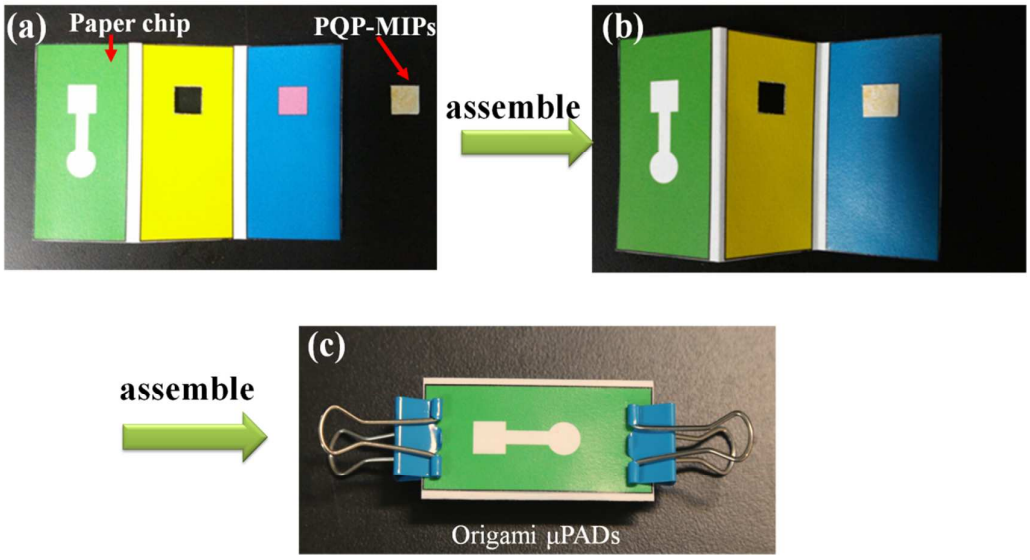


Fig S2. Infrared (IR) adsorption spectrum of (a) bare paper, (b) paper@QDs, (c) paper@QDs@PC-MIPs.



FigS3. Photograph of the quantum dot-based molecularly imprinted 3D origami paper-based microfluidic chip prepared on page of A4 size Whatman No.1 filter paper.



FigS4. (a) The component of paper chip and paper@QDs@PC-MIPs (PQP-MIPs). (b, c) Assembly of the origami μPADs. The dimensions of the chip are 5.5 cm × 2.7 cm, the sample reservoir is 6 mm in diameter, and the distance between the sample reservoir and detection area (8 mm × 8 mm) is 1.2 cm.

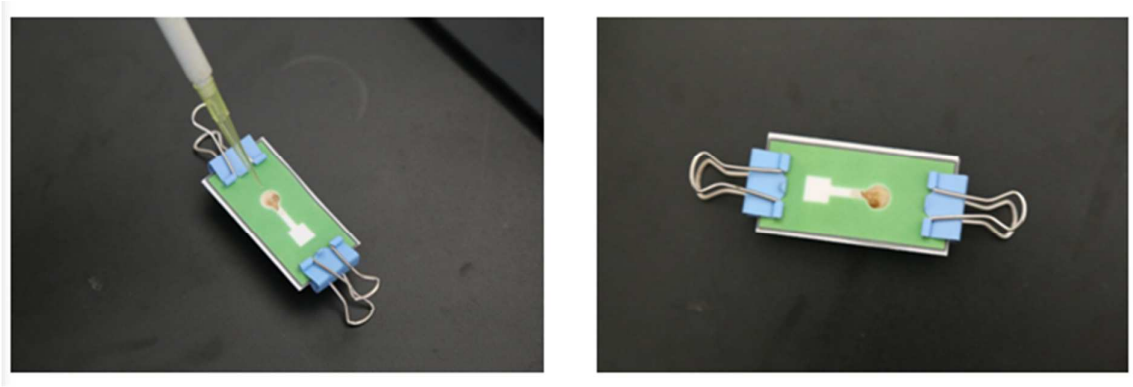


Fig S5 (a) We drop the dirty water sample on the 3D origami μPAD (b) The origami μPAD could realize the simple sample filter function

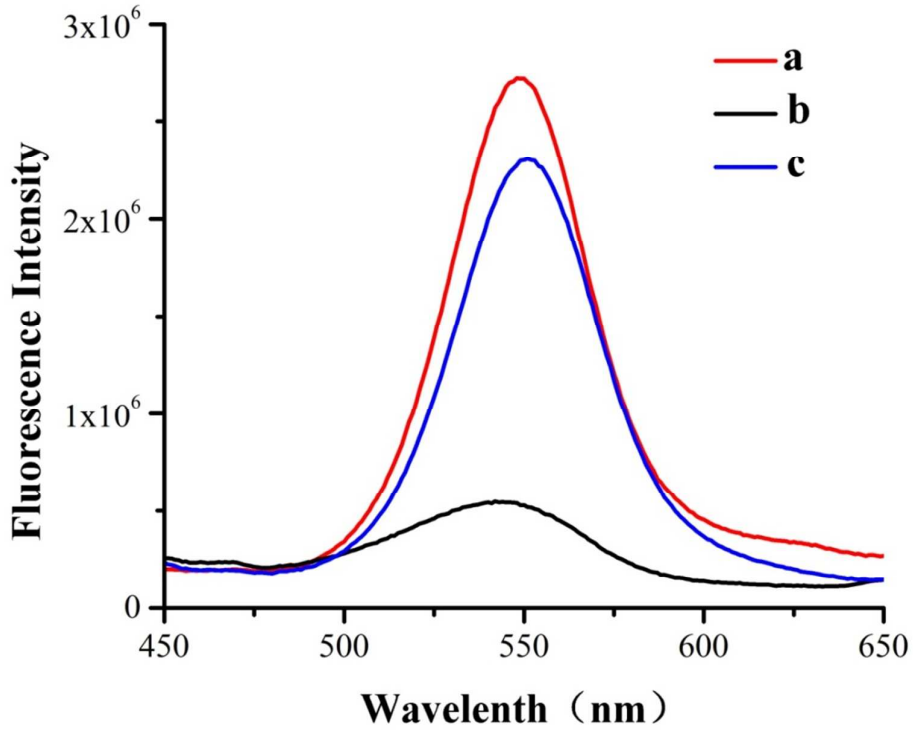


Fig S6. The fluorescence recovery curve after eluting PC template molecular. The fluorescence intensity of (a) paper@QDs@PC-NIPsμPADs (b) The PC template molecular were located in the MIP sites. (c) After eluting the PC template molecular and the fluorescence recovered remarkably. The template elution process was to rinse three times with 30 ml of 1% Triton X-100 solution by oscillating at 100 rpm for 30 mins and then rinsed three times with DI water.

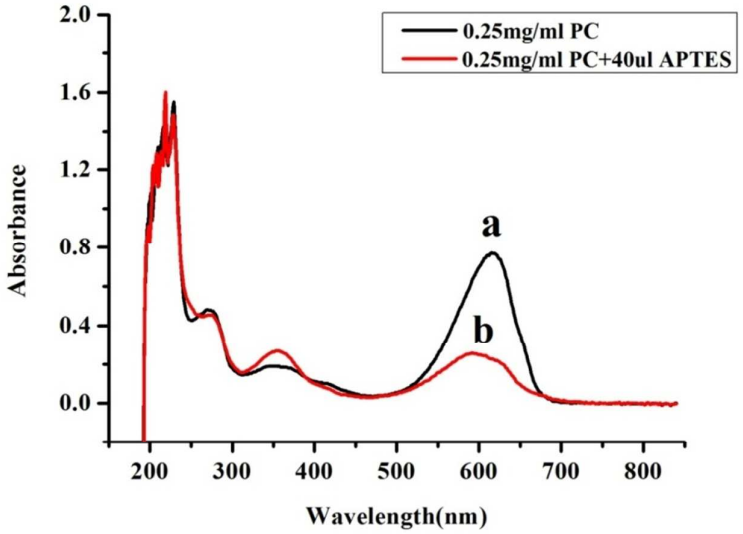


Fig S7. (a) UV-vis spectra for phycocyanin, (b) UV-vis spectra for addition of APTES and phycocyannin.

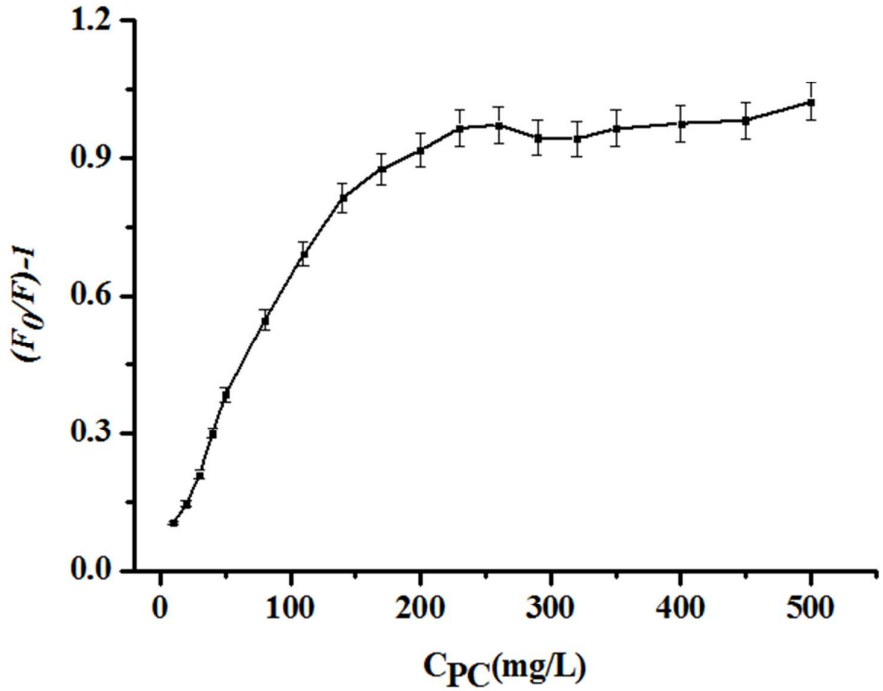


Fig S8. The dynamic equilibrium curve illustrated nearly all the PC was absorbed by the sensors if the concentration of PC is lower than 150 mg/L.

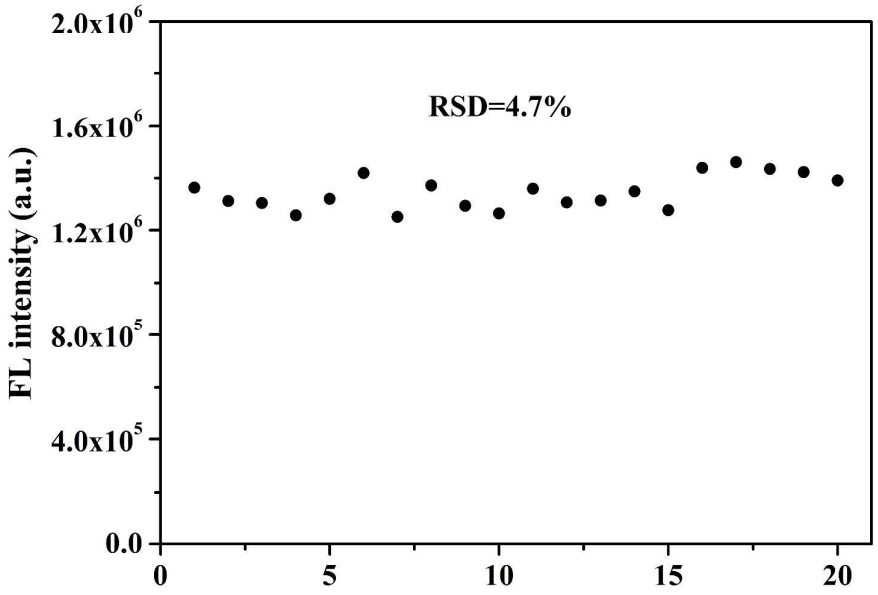


Fig S9. Fluorescence value determination for 20 different positions on the same piece of paper. The phycocyanin concentration is 30 mg/mL.

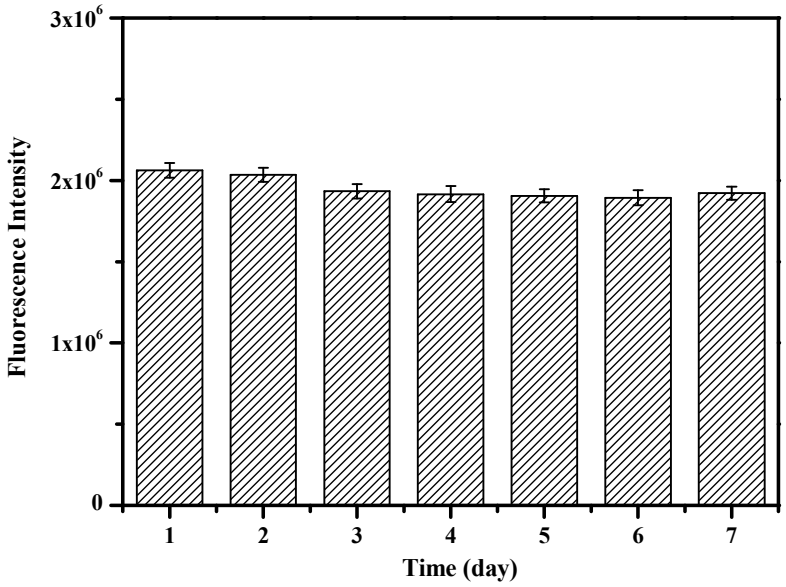


Fig S10. The curve of the fluorescence stability of five different paper@QDs@PC-MIPs μPADs during 7 days.