Electronic Supporting Information

Rewritable Multicolor Fluorescent Patterns for Multistate Memory Devices with High Data Storage Capacity

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Experimental section

Materials. Sodium tellurite (100 mesh, 99%), mercaptosuccinic acid (MSA), sodium borohydride (99.995%) and BPEI solution (50% in water, Mw 750 000) were purchased from Sigma-Aldrich. Cadmium chloride hemipentahydrate was obtained from Acros Oganics. Sodium citrate tribasic dihydrate was purchased from Fluka. All of the chemicals were of analytical grade and used without further purification. The water was deionized through a Millipore system.

Synthesis of CdTe QDs. Highly fluorescent MSA-capped CdTe nanocrystals were synthesized according to Bao's route.[1, 2] Freshly synthesized CdTe QDs with red, yellow and green emissions were used in following experiments. The molar concentration of QDs was determined based on its adsorption according to Peng's report.[3]

Characterizations. Surface morphologies of QDs adsorbed on a BPEI immobilized glass slide before and after the BPEI solution treatment were captured with tapping-mode AFM (SPM 3100, Veeco Instruments Inc., USA) at ambient condition. The section curves were analyzed with the Nanoscope V5.30 software.

The UV-vis and PL spectra were measured on HITACHI U-2800 double-beam system and scientific thermal NanoDrop 3300 fluorospectrometer with an illumination source at 365 nm. The PL spectra of glass immobilized QDs before and after BPEI solution treatment were collected using an Aminco Bowman II luminescence spectrometer (Thermo Electron, USA) with an illumination source at 350 nm.

Writing and erasing of fluorescent patterns. A PDMS mask with designed patterns was covered on a clean glass slide or a PDMS substrate. 0.01 mM QD solution was dropped on the mask and incubated in ambient air for 10 min. After washing with

deionized water, the fluorescent images were captured with a ScanArray GX Microarray Scanner under a 460 nm illumination. In the erasing step, the surface of the slide was covered by 1% BPEI solution for 15 min to decompose the QDs. The fluorescent pattern was removed and the regenerated surface was ready for next round of writing.

Fabrication of binary coded microarray data storage chip. The freshly synthesized QDs with red, yellow and green emissions were used for the microarray fabrication. After centrifugation at 6000 g for 10 min, the QDs were dispersed in a 0.01 M phosphate buffered saline containing 2.5% glycerol and 0.003% Triton-X 100 and then transferred to a 384-well microtiter plate. The contact printing process was performed using VersArray chipwriterTM (BIORAD) with telechem print head and steal microspotting pins. At 60% humidity, ~ 0.3 nL of sample per spot was delivered to the substrate. The images were acquired using a ScanArray GX Microarray Scanner under a 460 nm illumination.

Surface plasmon resonance (SPR) experiments. Real-time SPR binding curve was recorded using an autolab SPRINGLE SPR system (Eco Chemie BV, Netherlands). Fresh gold-evaporated glass disks were directly used in the test. Firstly, 100 μL of 1% BPEI solution was added into the cuvette and incubated at room temperature for 10 min to form a positively charged self-assembled monolayer on the gold surface. After washing with deionized water, 100 μL of 0.01 mM QD solution was injected into the cuvette to electrostatically adsorb QDs on the gold disk. Once the binding reached to the equilibrium, another 100 μL of 1% BPEI solution was added to decompose QDs and to generate a new active surface. Since the detection limit for the SPR test was around 4000

millidegrees of angle shift, two cycles were recorded to demonstrate the adsorption and the decomposition of QDs.

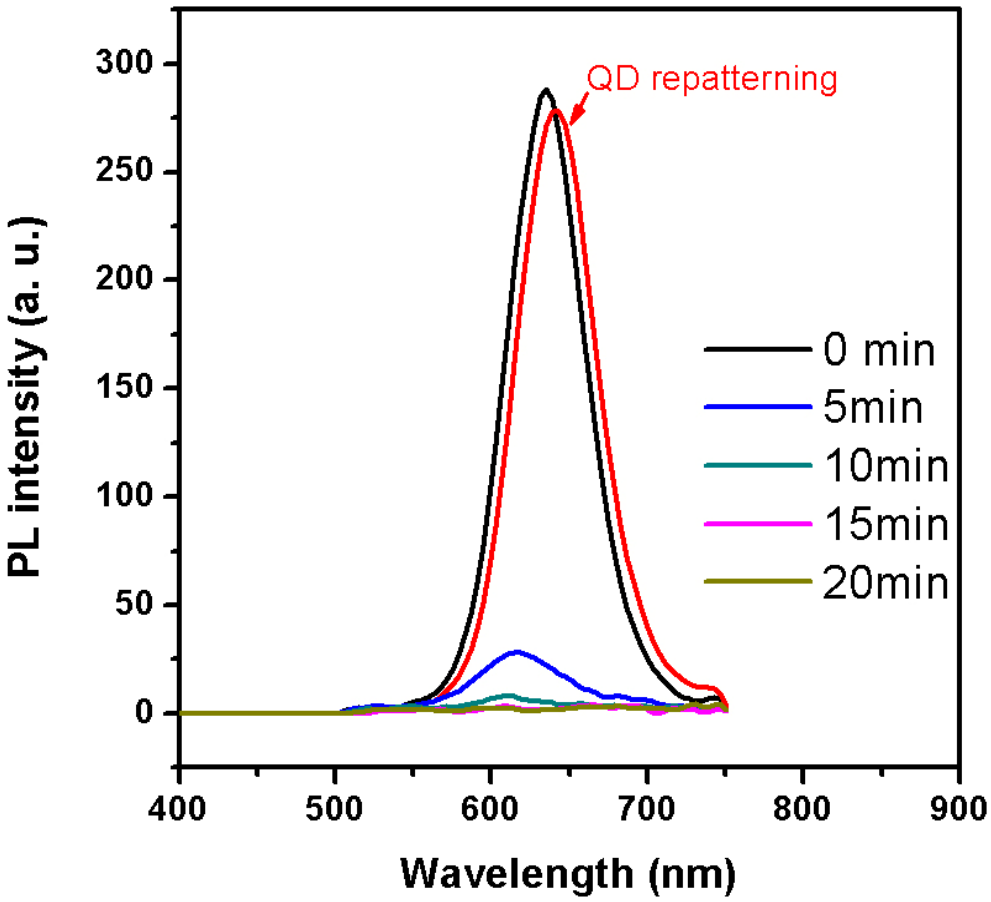

Figure S1. Time-dependent fluorescence extinguishing of surface-immobilized QDs.

In order to find the optimal time for erasing step, we investigated the time-dependent fluorescence extinguishing of surface-immobilized QDs. As shown in Fig. S1, the fluorescence obviously drops during the first 5 min. After 15 min, no fluorescence can be detected. The results indicate that the erasing step should last longer than 15 min. The blue shift occurred in the erasing step is consistent with the finding in PL measurement based on QD-BPEI mixtures. The fluorescence intensity of the re-patterned QDs is comparable to that of the original QD layer. Interestingly, there is a slightly red shift,

which may be due to the aggregation of QDs adsorbed on the regenerated surface. Since the slight shift is only 3 nm, it will not affect the QD emission color and the final images.

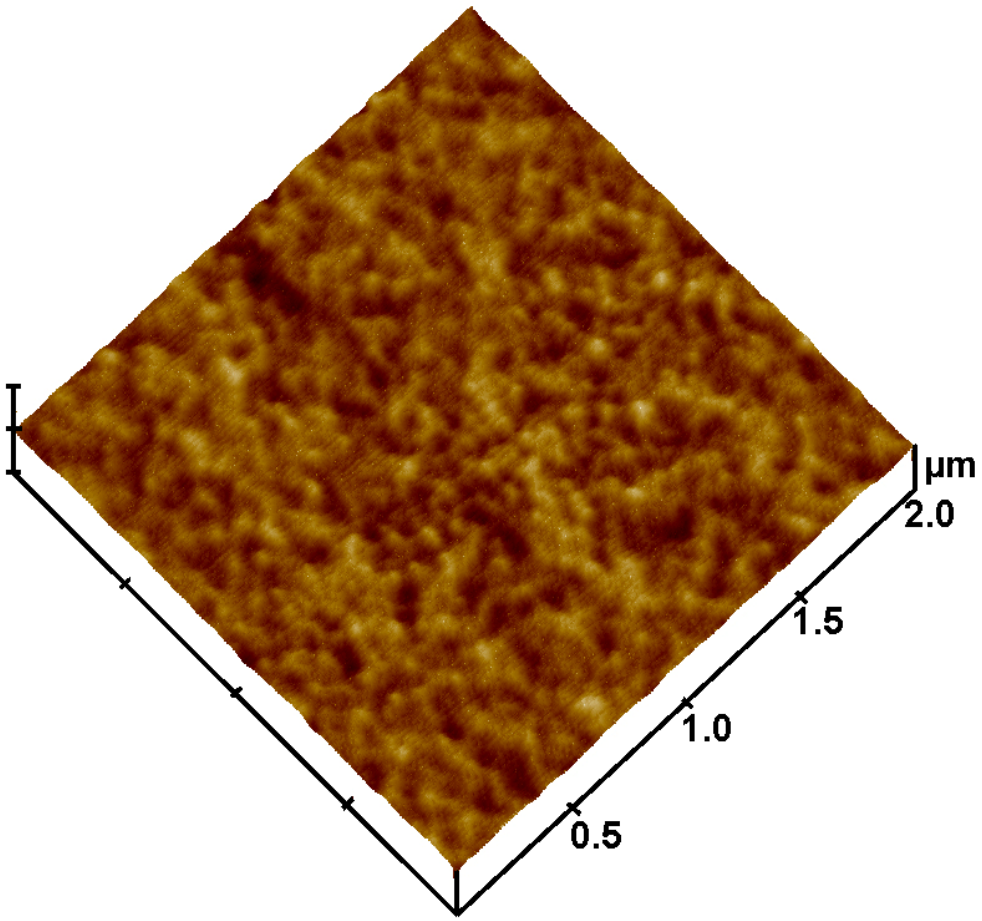

Figure S2. Surface morphology of a BPEI-modified glass slide. (Z scale=10 nm)

The surface morphology of a BPEI-immobilized glass slide before QD adsorption is shown in Fig. S2. In comparison to the AFM images in Fig. 1a, the BPEI-modified surface is quite smooth with an image roughness of 0.28 nm. After immersion in the QD

solution, a number of islands appear on the surface and the image roughness increases to 3.83 nm (Fig. 1a), indicating the adsorption of QDs on the BPEI-modified surface.

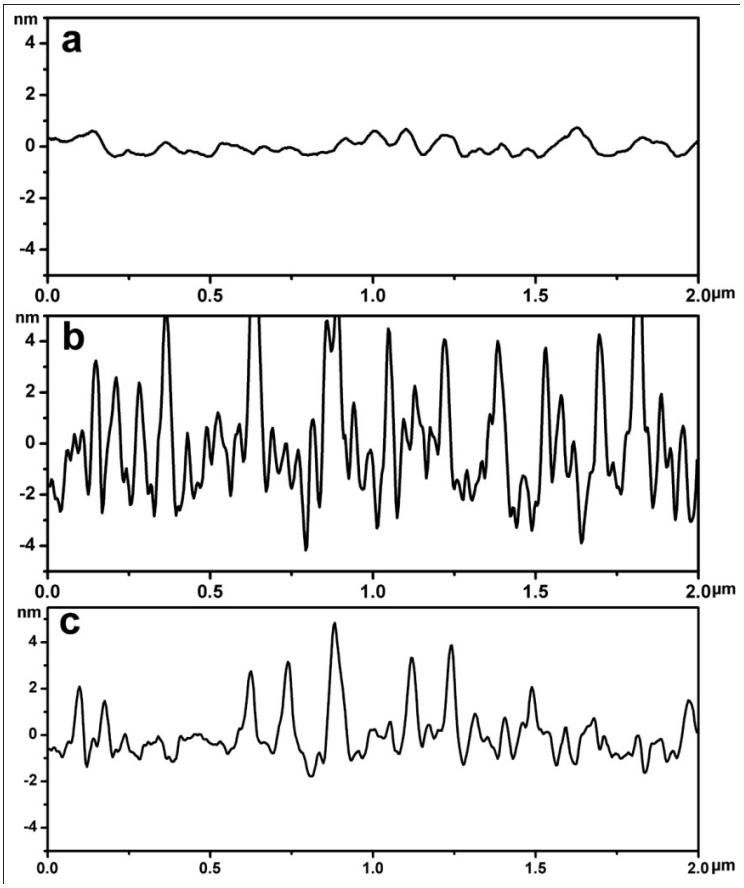

Figure S3. Section curves of the AFM images of the BPEI-modified glass slide (a), QDs adsorbed on the BPEI-modified glass slide before (b) and after (c) BPEI solution treatment.

In addition to the surface morphologies and roughness changes, the section curves in Fig. S3 clearly show the size and density alteration of the surface-adsorbed QDs in the writing and erasing cycles. The dot heights range from 3 to 5 nm that matches the size of QD, suggesting the adsorption of QDs (Fig. S3b). After BPEI solution treatment, most of the dot sizes reduce to 1-2 nm and the frequency of the peaks also significantly decreases.

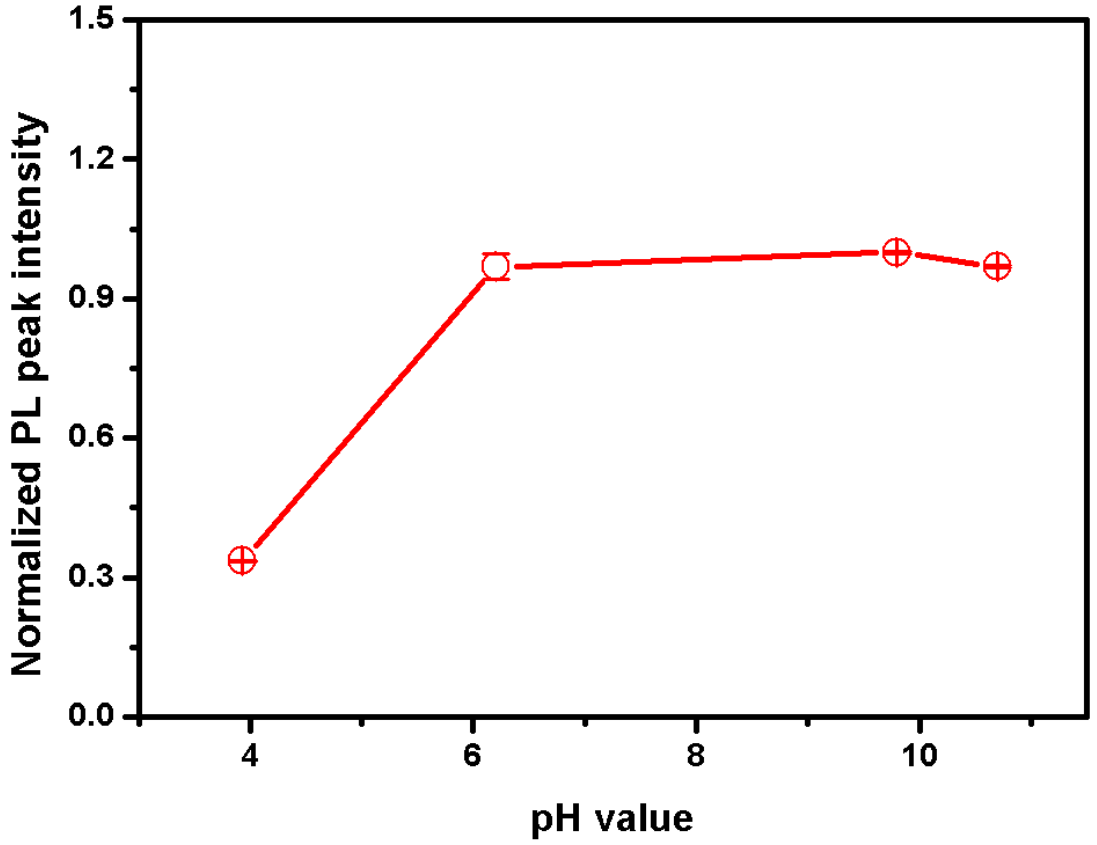

Figure S4. Effects of pH value on the fluorescence intensity of CdTe QDs

The stability of the synthesized CdTe QDs in different pHs is shown in Fig. S4. There is no significant change on the fluorescence intensity with the pH increasing from 6.1 to 10.4. Hence, pH 6.5, 8.6 and 10.3 are applied to adjust the protonation/deprotonation degree of BPEI.

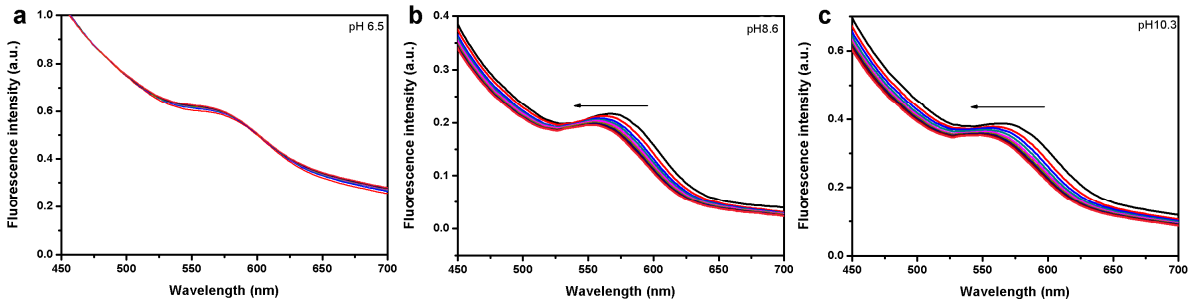

Figure S5. UV-vis spectra of QDs exposed to 1% BPEI solution with pH of 6.5 (a), 8.6 (b) and 10.3 (c).

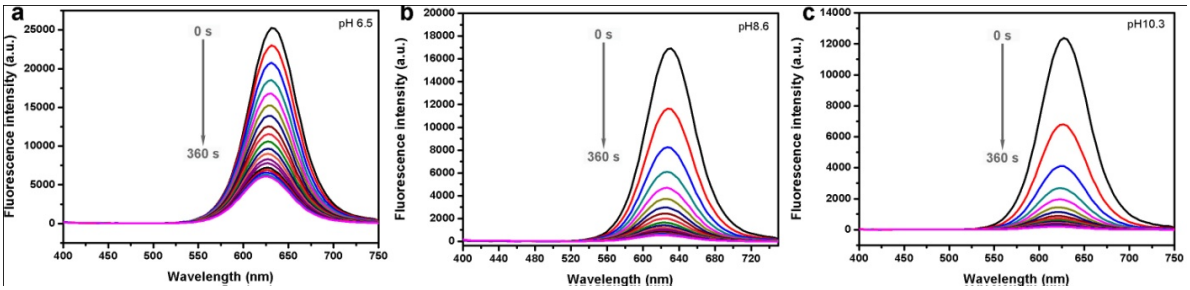

Figure S6. PL spectra of QDs exposed to 1% BPEI solution with pH of 6.5 (a), 8.6 (b) and 10.3 (c).

It has been reported that the dissociation constant (K_a) of BPEI is ~8.56. By simply adjusting the pH of solution, we can obtain BPEI molecules with different protonation degrees. The blue shift of UV-vis spectra and the fluorescence intensity decrease of PL spectra at pH 6.5 are not as significant as those at pH 8.6 and 10.3, since the protonation degree of BPEI at pH 6.5 is the highest among three samples. The PL extinguishing effect and the blue shifts of UV-vis and PL spectra are more significant in BPEI solution with higher alkalinity. Because the chelating activity depends on the

protonation/deprotonation of nitrogen atoms, the results indicate that the chelating ability of BPEI may be the cause of the decomposition of QDs.

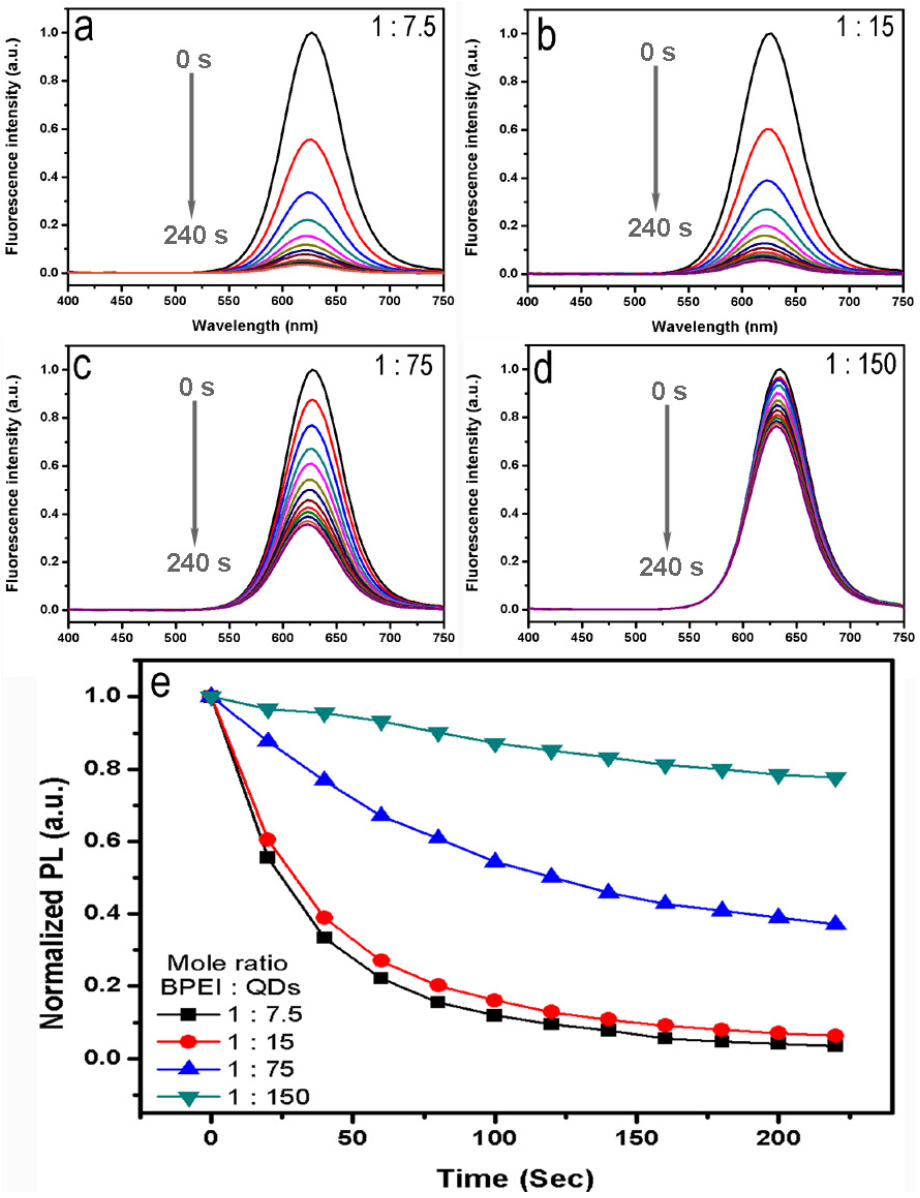

Figure S7. Effect of BPEI to QDs mole ratio on extinguishing efficiency. Time-dependent extinguishing effects at mole ratios of 1 : 7.5 (a), 1 : 15 (b), 1 : 75 (c) and 1 : 150 (d), respectively. (e) Comparison of time-dependent extinguishing effects at different ratios.

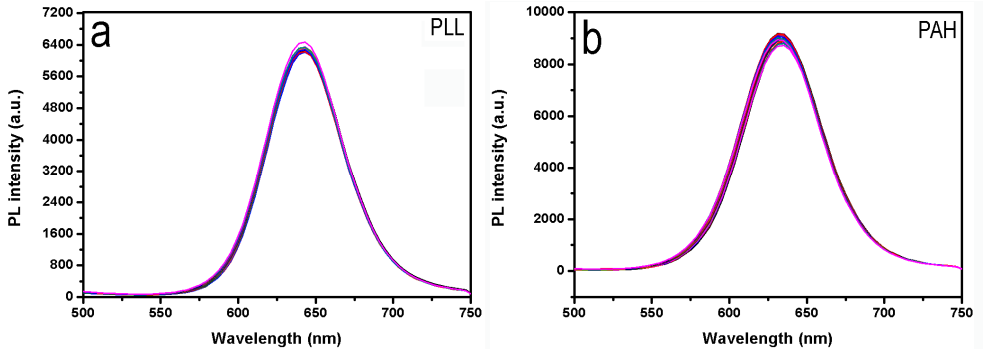

Figure S8. PL spectra of QDs exposed to 1% poly-L-lysine (PLL) solution (a) and 1% Poly(allylamine hydrochloride) (PAH) solution (b).

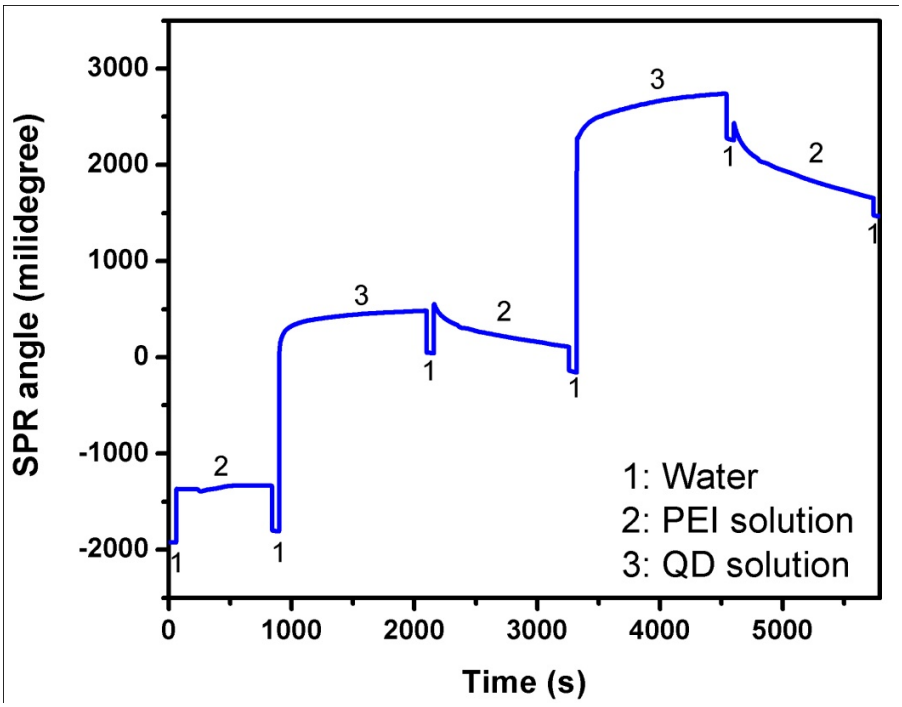

Figure S9. SPR real-time binding curve of the QD writing and erasing process.

Firstly, the bare gold disk was immobilized with a layer of BPEI molecules. The slight enhancement of the SPR angle suggests the successful adsorption of BPEI molecules on the surface. Then, two rounds of writing and erasing were real-time monitored. The

significant increases of SPR angle caused by the adsorption of a large amount of QDs verify that the electrostatic force can be used for fluorescent information patterning. Differently from the adsorption of BPEI on bare gold disk, the decrease of SPR angle occurs in the BPEI solution, which may imply the decomposition of QDs in the erasing steps. The SPR result together with the surface morphologies and the spectral data clearly shows that BPEI-QD system can be applied for reversible writing and erasing.

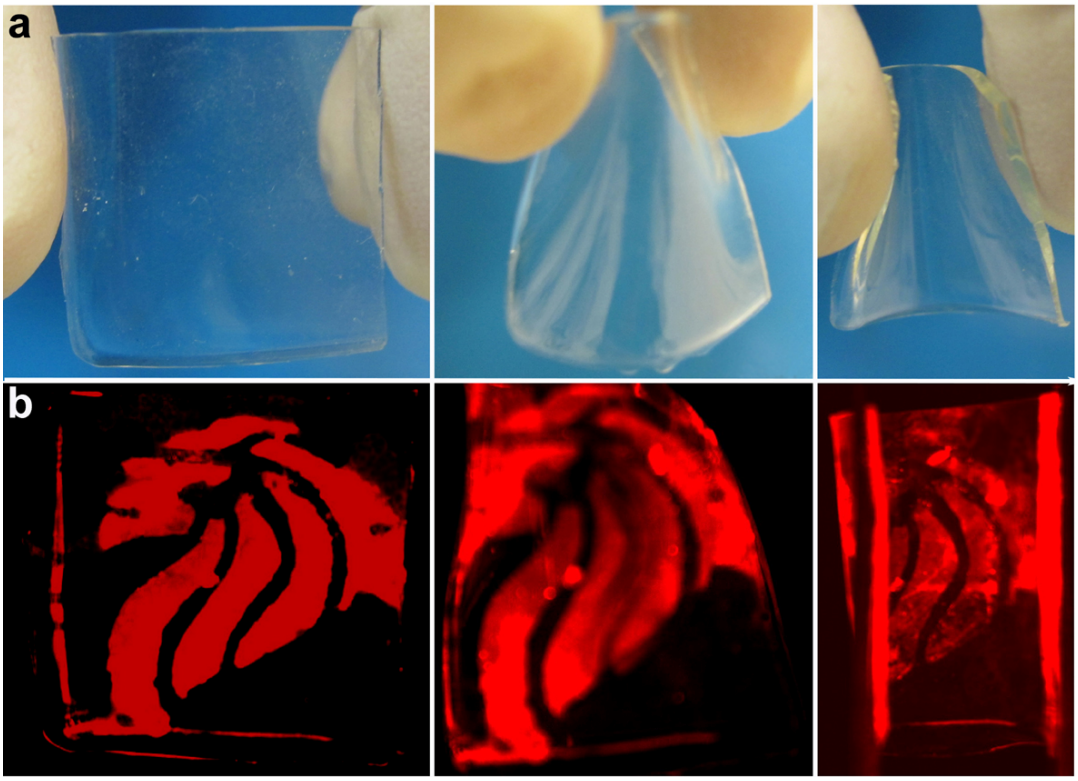

Figure S10. QDs patterned on a flexible and bendable PDMS substrate. (a) Pictures taken under room light; (b) Fluorescent images captured with a scanner under irradiation.

The flexibility of the substrates that carry the secret information is very critical for their practical applications in secure communications. A PDMS membrane with the thickness of 2 mm was employed as the substrate. As illustrated in Fig. S10, the QD fluorescent

pattern can be written on the PDMS surface and the bending of substrate does not affect the fluorescent information.

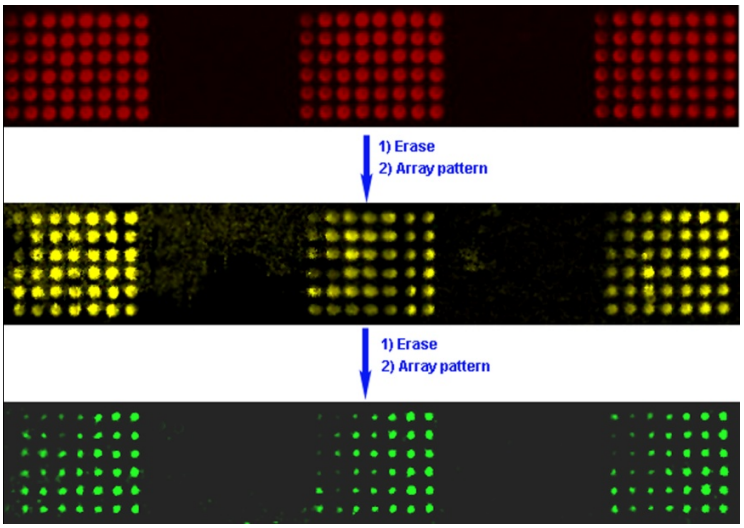

Figure S11. Microarrays fabricated with red, yellow and green QDs via QD writing-BPEI solution erasing cycles.

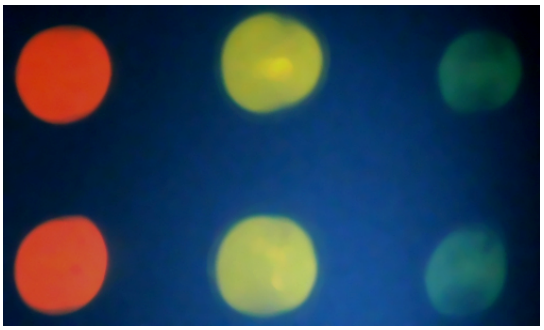

Figure S12. Fluorescent micrograph of a QD patterned multicolour microarray.

QD-based microarrays with red, yellow and green emissions were fabricated using the BPEI-QD system. Before the patterning step, the glass slide was immersed in a 1% BPEI solution for 10 min to functionalize the surface with positive charges. Then, the QDs printing buffer were transferred to the surface using a microarray chipwriter. Since the printing buffer containing glycerol that prevents the evaporation of water, the printed slide was incubated in ambient air for 20 min without drying. After a washing step, the

QD microarrays with red-colour emission are obtained. The BPEI immersing and QD microarray patterning were repeated to get the yellow and green emission microarrays.

References

[1] Bao, H. F.; Wang, E. K.; Dong, S. J. *Small* **2006**, *2*, 476-480.

[2] Bao, H. F.; Cui, X. Q.; Li, C. M.; Zang, J. F. *Nanotechnology* **2007**, *18*, 455701.

[3] Yu, W. W.; Qu, L. H.; Guo, W. Z.; Peng, X. G. *Chem. Mater.* **2003**, *15*, 2854-2860.