Supporting Information

Photoelectric Conversion Switch Based on Quantum Dots with i-motif DNA Scaffolds

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1. Materials:

The gonucleotides listed in Table S1 were synthesized by TaKaRa Biotech (Dalian, China), and their CSs were bought from SBS Genetech (SBS, Beijing). 2-Mercaptoethanol (99%), EDC (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide) and sulfo-NHS (NHSS, N-hydroxy-sulfosuccinimide) ester were purchased from Sigma Company. Methoxypolyethylene glycol amine 750 (PEG-NH_2 750) was bought from Fluka. PBS buffer (pH 4.5, 5.0 or 8.0) was prepared with ultrapure MilliQ water (resistance larger than 18 MΩ·cm). Gold substrates were prepared on silicon wafers. The silicon wafers were cleaned by acetone and deionized water, and then coated with a chromium adhesion layer (～1 nm) and Au layer (＞20 nm) in turn by Sputter Machine.

DNA name	sequence
Motor DNA	5'-SH-TGTTTTCTTCCCTAACCCTAACCCTAACCC-NH_2-3'
Motor DNA-CS	5'-GTGTTAGTGTTAGTGTTAGTGAAGAAAACA-3'
Control DNA	5'- HS-TGTTTTCTTACTATGCTGTTACTCTGACTC-NH_2-3'
Control DNA-CS	5'-GAGTCAGAGTAACAGCATAGTAAGAAAACA-3'

Table S1 Sequence list of DNA used in this study. CS is abbreviation of complementary strands. The four bases Ts underlined in the Motor DNA-CS sequence show the DNA mismatch.

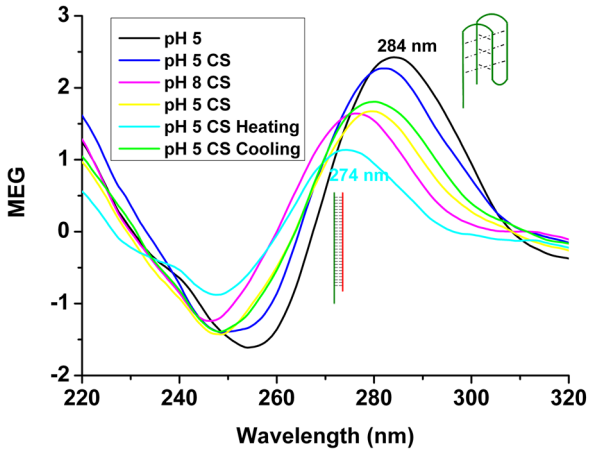


Fig. S1 CD spectra of motor DNA and its mismatched CS in PBS when the pH value of the solution is changed. Peak at 284 nm is shifted to 274 nm when the pH value is

changed from 5.0 to 8.0, indicating that the conformation of motor DNA has transformed from the quadruplex strands to the double-helix structure.

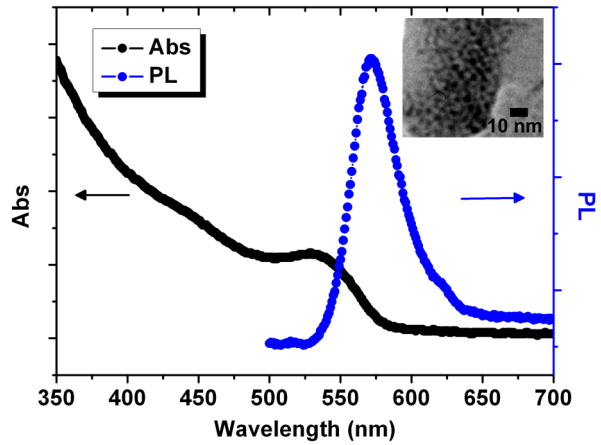


Fig. S2. UV-vis absorption spectra (the black) and PL emission spectra (the blue) of the prepared CdSe/ZnS core-shell QDs in PBS buffer (pH 7.4). They have maximum emission at about 572 nm and broad absorption region, indicating the good efficiency of solar energy collection. Calculations upon the empirical formula[S1] suggest that the average diameter of QDs is around 3 nm. The inset shows its TEM image, which confirms the dimension of the prepared QDs.

(S1) W. W. Yu, L. Qu, W. Guo, X. Peng, *Chem. Mater.* 2003, **15**, 2854.

2. Assembly of QDs-DNA-Au conjugates:

i-motif motor DNA and control DNA as listed in Table S1 were immobilized on gold coated silicon wafer through thiol-gold interactions. Firstly, the Au surface was incubated with the solution of the motor or control DNA molecules (1 μM in PBS, pH 4.5) for 12h at room temperature, then immersed in 2-mercaptoethanol solution (1 mM in PBS) at the same pH for about 15 minutes to remove the nonspecifically attached DNA and simultaneously to eliminate the steric hindrance among attached DNA molecules. After removal of 2-mercaptoethanol by thoroughly rinsed with PBS solution (pH 4.5), the amino-terminated surface was immersed into the PBS (pH 7.4) solution containing CdSe/ZnS QDs (about 2.5 μM), EDC (1 mM), and NHSS (0.5 mM). Both EDC and NHSS were used as coupling reagents to activate the COOH groups of MPA stabilizers, leading to the cross-linking reaction between QDs and DNA molecules. PEG-NH_2 (0.25 mM) was also employed to graft PEG molecules onto the QDs surface to protect them from possible pH-sensitive change in following experiments[S2]. The obtained QDs-DNA-Au assembly was served as the work electrode in the following photoelectric chemical analysis.

(S2)*(a)* H. T. Uyeda, I. L. Medintz, J. K. Jaiswal, S. M. Simon, H. Mattoussi, *J. Am. Chem. Soc.* 2005, **127**, 3870; *(b)* K. Susumu, H. T. Uyeda, I. L. Medintz, T. Pons, J. B. Delehanty, H. Mattoussi, *J. Am. Chem. Soc.* 2007, **129**, 13987.

3. Characterization

UV and PL spectra of CdSe/ZnS QDs were obtained by using U-3010 spectrophotometer (HITACHI) and FluoroMax-4 spectrofluorometer (HORIBA YOBIN YVON), respectively. As Fig. S3 demonstrated, the i-t characteristics of the samples were measured using an electrochemical analyzer (CHI630B, Chenhua Instruments Co., Shanghai) under 100 $mW \cdot cm^{-2}$ irradiation of solar-simulator illumination (CMH-250, Aodite Photoelectronic Technology Ltd., Beijing) at room temperature. The spectrum of the solar simulator was shown in Fig. S4. X-ray photoelectron spectroscopy (XPS) data were attained with AXIS Ultra by Kratos Analytical (UK) using monochromatic Al Kα X-rays (1486.7 eV). X-ray source of 15 kV and 12 mA for Neutralizer gun was applied (1.85 A and 3.15 V). The operating pressure was about 10^{-7} Pa. All peaks were referenced to C 1s (CHx) at 284.8 eV in the deconvoluted high resolution C 1s spectra, and the analysis software used was provided by the manufacturer.

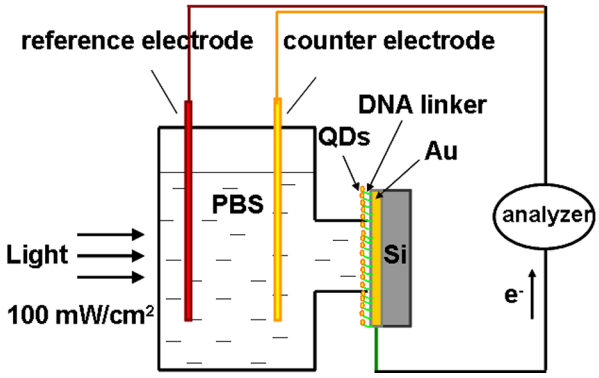


Fig. S3. Scheme of i-t curves measurement system. A solar simulator is used as light source. The Pt and calomel electrodes are employed as counter and reference electrodes, respectively, with PBS buffer solution as electrolyte.

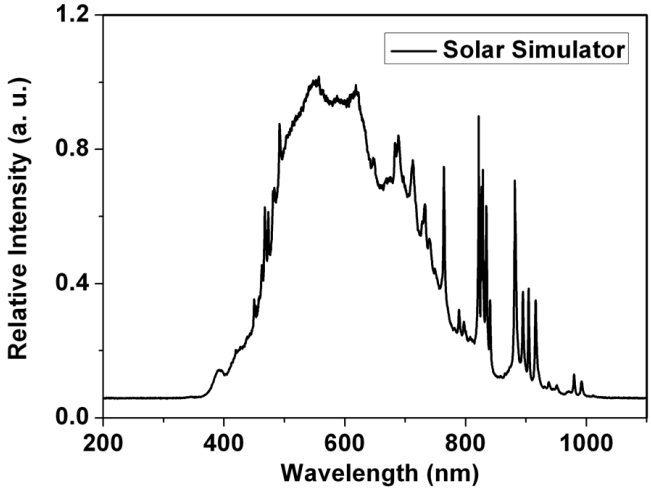


Fig. S4 The spectrum of the solar simulator employed in our experiment.

4. XPS element analysis

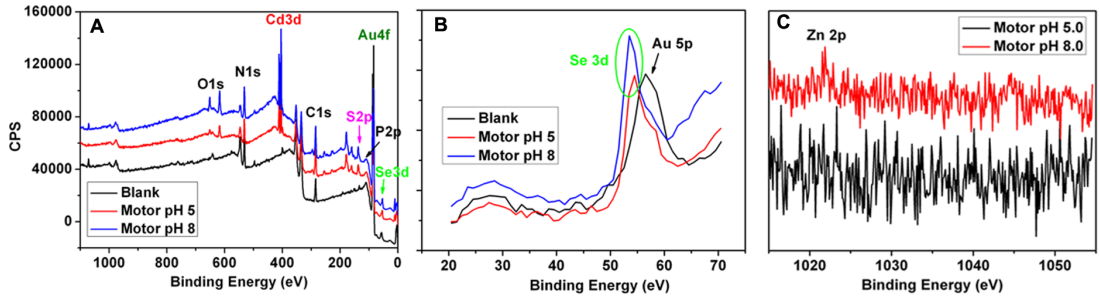


Fig. S5 XPS spectra of the prepared electrodes' surfaces. (A) The black curve (blank sample) only shows the signals of elements C, N, O, P, S (from DNA) and Au (from substrate), and no peaks of Cd and Se elements appear. However, the Cd and Se peaks with enhanced S and weakened Au signals are demonstrated obviously for the red (pH 5.0) and blue ones (pH 8.0) (See Table S2). It should be note that the peak of Zn is not labeled in the spectra, because it is hard to be detected due to its high energy (Zn 2p/3 peak at 1022 eV), and only in solution of pH 8.0 there appears a little signal in the single element analysis (C). (B) Detailed comparison of Se element. There is only a peak of Au 5p in the blank sample, whereas the peak of Se 3d complexes with Au 5p is emerged after conjugation with QDs.

Name	% Conc.		
	Blank	pH 5.0	pH 8.0
C 1s	47.4	46.5	47.6
O 1s	13.6	11.7	13.2
N 1s	5.8	4.5	4.3
P 2p	12.6	12.1	13.4
S 2p	0.9	5.1	4.6
Au 4f	19.7	12.8	8.3
Cd 3d	—	4.3	5.7
Se 3d	—	3.0	2.9

Table S2 The analysis of element percentage content. "Blank" corresponds to the blank sample without cross-linking of QDs, while pH 5.0 and pH 8.0 stand for the motor devices at these two pH values. Note that there is a considerable uncertainty for the measurement of Se element percentage, because of the low detection sensitivity for Se 3d at 54.1 eV and its complex with Au 5p (Figure S4).

5. QCM measurement

Quartz crystal microbalance (QCM) can sensitively detect interfacial mass changes. Quantitative analysis is possible via the Sauerbrey equation for measurements taken under vacuum condition (or approximately in air):

$$\Delta mass = -\Delta f_n \frac{C}{n} \qquad (1)$$

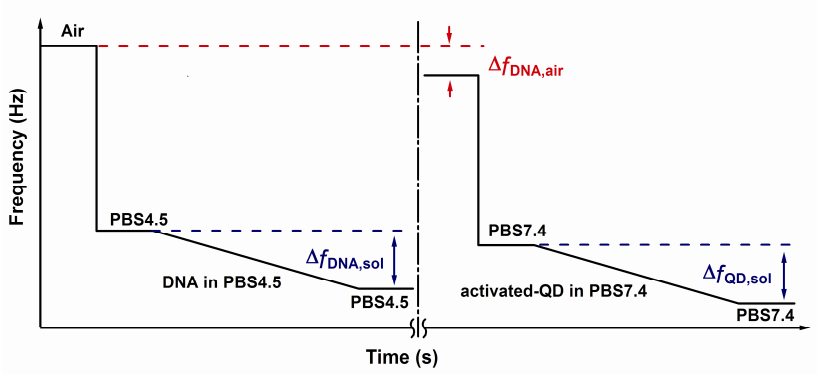
where Δmass (ng cm^{-2}) is the area averaged mass loading, Δf_n (Hz) is the measured frequency change due to the added mass, n is the overtone number (n = 3 in this paper), C = 17.7 ng cm^{-2} Hz^{-1} is the constant for a crystal with a fundamental resonance frequency 5 MHz.

Quantitative analysis for data from liquid environment is complicated because QCM measures wet mass, i.e., the deposited mass, the entrapped liquid, and the viscoelasticity changes can be reflected as frequency changes.[S3,S4] For these reasons, the Sauerbrey equation is no longer valid. Fortunately, the system studied here has negligible viscoelasticity contribution because the DNA monolayers are sufficiently thin. Several publications have suggested the entrapped water usually takes half of the wet mass,[S3-S5] thus we applied equation (2) to estimate dry mass from frequency change measured under wet condition.

$$\Delta mass = \frac{C}{n}\frac{-\Delta f_{n,Sol}}{2} \qquad (2)$$

Both the immobilization of i-motif DNA and QDs were followed online by a QCM. In a typical run, an UV-ozone cleaned, gold-coated QCM chip was firstly loaded to a QCM sensor to measure its absolute resonating frequency (Scheme S1). Second, PBS (pH = 4.5) was pumped over the QCM chip to establish the baseline as the reference for the bare chip. Third, the solution of DNA (i-motif DNA or control DNA in PBS

pH = 4.5) was introduced and the immobilization of DNA on the chip was monitored online. After 60 min, the DNA solution was replaced by PBS and the frequency change, $\Delta f_{\text{DNA, Sol,}}$ was read directly from the QCM curve. Forth, the chip was then dried and re-loaded to a dry QCM chamber to measure its absolute frequency again. The frequency difference between after and before DNA immobilization was defined as $\Delta f_{\text{DNA, Air.}}$ Fifth, PBS (pH = 7.4) was pumped over the new DNA-coated QCM chip to establish a baseline for QDs immobilization. The EDC/NHSS activated QDs in PBS (pH = 7.4) was introduced to the QCM chamber and the frequency decrease due to QDs immobilization was followed online (~ 4h). The frequency change, $\Delta f_{\text{QDs, Sol,}}$ was read directly from the QCM curve. We did not measure the $\Delta f_{\text{QDs, Air}}$ because QDs are not so stable in air.



Scheme S1. Illustration of experimental design, details are showed in the above text.

	Motor DNA	**control DNA**
$\Delta f_{\text{DNA, Air}}$ **(Hz)** [a]	44.4	45.9
Δ*mass* (ng cm^{-2}) [b]	262.5	270.9
Density(cm^{-2}) [c]	1.8×10^{13}	1.8×10^{13}
$\Delta f_{\text{DNA, Sol}}$ **(Hz)** [a]	68.4	93.1
Δ*mass* (ng cm^{-2}) [d]	201.6	274.9
Density(cm^{-2})	1.4×10^{13}	1.8×10^{13}

[a] triplicate, SE < 10% for $\Delta f_{\text{DNA, Air}}$ and SE < 5% for $\Delta f_{\text{DNA, Sol}}$, [b] calculated from equation (1), [c] the molar mass of DNA was estimated to ~9KD, [d] calculated from equation (2).

Table S3. Density estimations of immobilized DNA molecules from frequency changes measured by QCM.

	Motor DNA	control DNA
$\Delta f_{QDs,\ Sol}$ (Hz) [a]	116.1	117.3
$\Delta mass$ (ng cm^{-2}) [b]	342.8	346.4
Density(cm^{-2}) [c]	2.3×10^{13}	2.3×10^{13}

[a] triplicate, SE < 5%, [b] calculated from equation (2), [c] the mass of one QD was estimated to be 2.88×10^{-11} ng.

Table S4. Density estimation of immobilized CdSe/ZnS QDs from frequency changes measured by QCM.

(S3) L. Fu, X. Chen, J. He, C. Xiong, H. Ma, *Langmuir* 2008, **24**, 6100.

(S4) J. He, Y. Wu, J. Wu, X. Mao, L. Fu, T. Qian, J. Fang, C. Xiong, J. Xie, H. Ma, *Marcromolecules* 2007, **40**, 3090.

(S5) X. C. Zhou, L. Q. Huang, S. F. Y. Li, *Biosensors & Bioelectronics* 2001, **16**, 85.

6. Measurement of the photoelectric response of control device

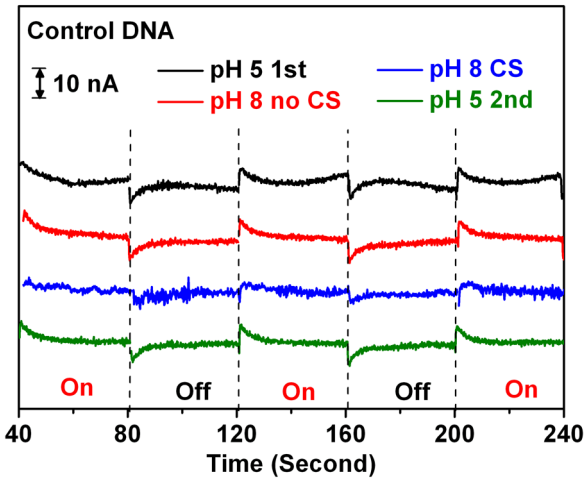


Fig. S6. I-t curves of control device at different pH values. There is no obvious change of its switching current while the pH value of solution is oscillated, because the conformation of control DNA does not change with pH value.