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# Effective construction of AuNPs-DNA system for the implementation of various advanced logic gates

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**Table S1** Sequences of the oligonucleotides used in this work.

| Name | DNA Sequence (from 5' terminal to 3' terminal) |
|---|---|
| $P_{EN1}$ | AAAAA AAAAA TTTT ACTGC ATGAG ATTTT GGACA T |
| F-$DNA_{EN1}$ | TACGAAGATGTGGAAAATCTCTAGTAGT |
| IN1 | ACTGC TAGAG ATTTT CCACA TCTTCGTA |
| IN2 | TAATA TAATT TAAT |
| $P_{EN2}$ | AAAAA AAAAACAACC TTCCA CATTCT ACT CCCCC TTT CCCCC TTT CCCCC TTTCCCCC |
| F-$DNA_{EN2}$ | GTCGAAGTGT AGTTTGTGGTTGGTTG |
| IN1' | TAATGTAATGTAAT |
| IN3' | CAACC AACCA CAACT ACTCTTCGAC |
| IN4' | CAACC AACCA CAACT ACTCTTCGAC GGGT GGGTGGGT GGG |
| $P_{HA}$ | AAAAA AAAAA TTT GGAATAGGAA |
| F-$DNA_{HA}$ | TTCCT ATTCC TACG |
| INA | ACCAC CGTAGGAATA TACGATGGGTGGG |
| INB | GGGTGGG T CGTAGGAATA CTACGGTGGT |
| $P_{HS}$ | AAAAA AAAAA TTT GGAATAGGAA |
| F-$DNA_{HS}$ | GGGT TTCCT ATTCG TACG |
| INA' | ACCAC CGTACGAATA GCGAT |
| INB' | CGTACGAATA GGAC GGGTGGGTGGGT |

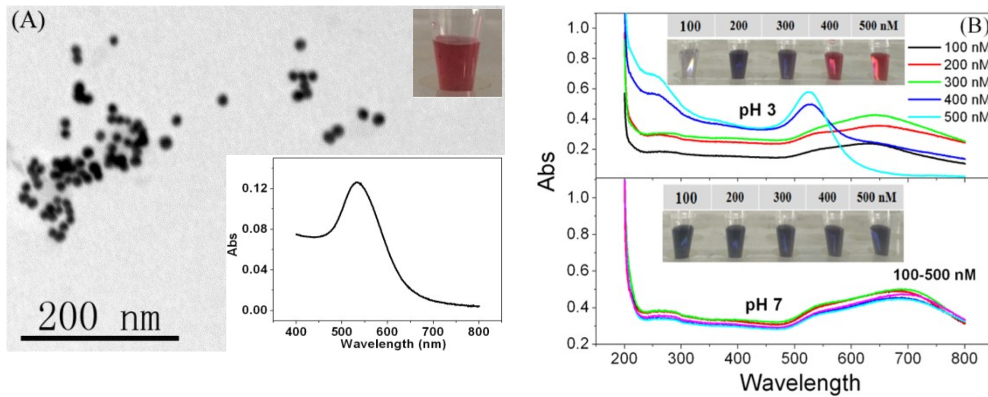


**Fig. S1** (A) The TEM image of AuNPs with the size of around 13 nm, insets are the adsorption spectrum and color display of AuNPs. (B) The comparison of absorption spectrum and color display for polyA-ssDNA (from the concentration of 100 nM to 500nM) protected AuNPs in pH 3 and pH 7.

We have synthesized the AuNPs with great desperation of wine red color and the adsorption peak at 525 nm. And then we have successfully conjugated a certain concentration polyA-DNA with AuNPs to great protect AuNPs from aggregation in the pH value of 3. On the contrary, the polyA-DNA cannot protect AuNPs from aggregation in pH 7.

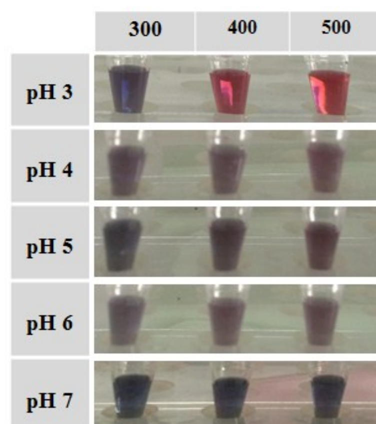


**Fig. S2** The color contrast description of polyA-DNA adsorbed on the surface of AuNPs to protect it in order to avoid integrating in the pH 3-7. From the figure we can see that, only in the pH 3 solution can the polyA-DNAgreat protect AuNPs.

we have fabricated the conjugation of AuNPs and polyA-DNA with great desperation of wine red color for the certain concentration of polyA-DNA can adsorbed on the surface AuNPs to protect it from aggregation in a short time at pH 3. The aggregation state of polyA-DNA modified AuNPs in other pH values, pH 4, 5, 6 and 7, as contrast experiments were shown in Fig, S1, which shows very well that only in pH 3 can polyA-DNA great protect AuNPs in a certain concentration of P-DNA sequence.

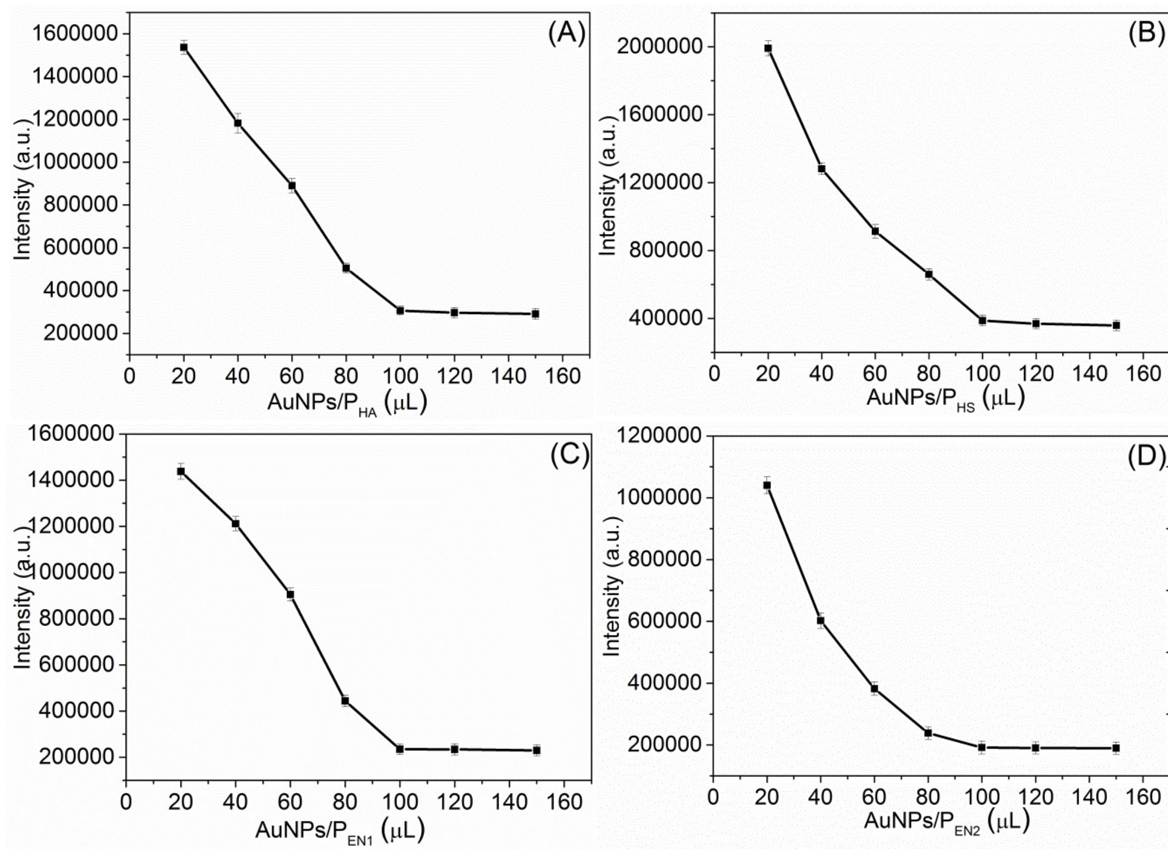


**Fig. S3** The optimization of volume of AuNPs that was protected by polyA-DNA in (A) half adder; (B) half subtractor; (C) 2:1 encoder and (D) 4:2 encoder. The optimum conditions of AuNPs protected by polyA-DNA used in various logic operations were all 100 μL.

To obtain the optimization of volume of AuNPs that was protected by polyA-DNA in half adder, half subtractor, 2:1 encoder and 4:2 encoder, we have modified the polyA-DNA in a certain concentration with FAM in different logic gates, for almost 100μL AuNPs in half adder, half subtractor, 2:1 encoder and 4:2 encoder can effectively quench the fluorescence of FAM when the polyA-DNA was conjugated to AuNPs. So the optimum conditions of AuNPs protected by polyA-DNA used in various logic operations were all 100 μL for the experiments.

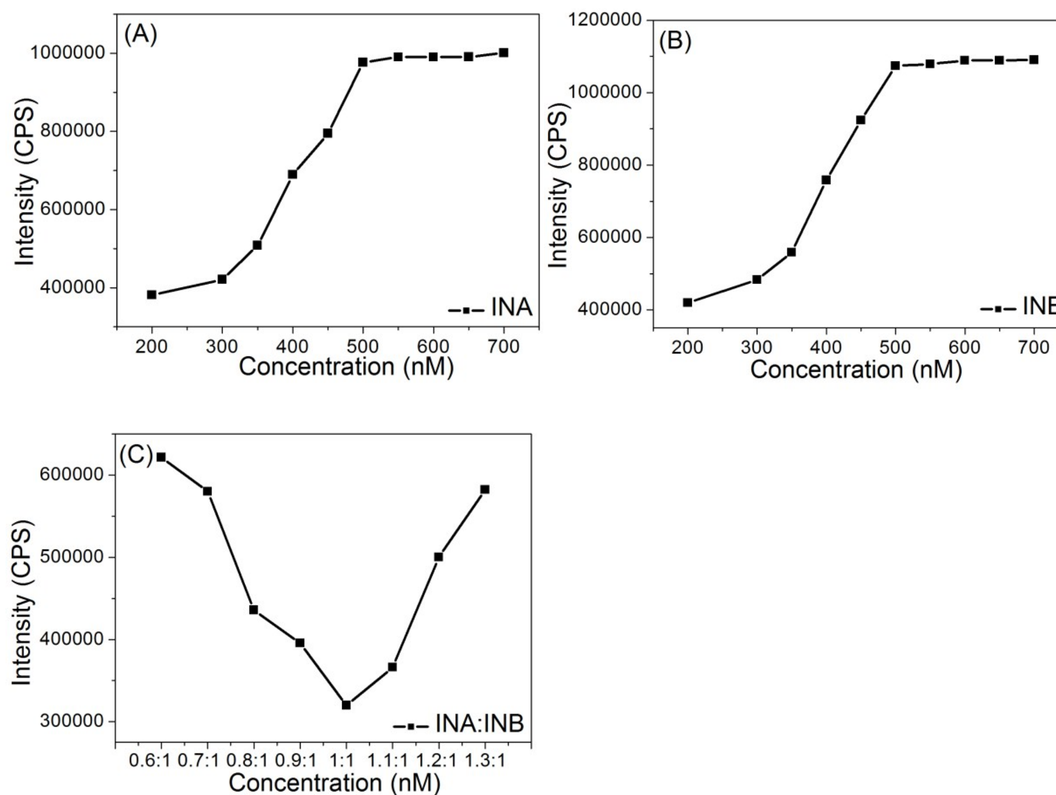


**Fig. S4** The FAM fluorescence response of AuNPs/$P_{HA}$/F-$DNA_{HA}$ complex with increasing the concentration of INA (A), INB (B) and INA:INB (C).

The fluorescence of FAM is generally recovered and reaches a platum with increasing the concentration of INA (A), INB (B). So 500 nM was used for each input to operate the half adder logic gate. The fluorescence of FAM is generally decreased when the concentration ratio is close to a proper value in (C), that is because each of the two inputs can hybridization and leave the F-$DNA_{HA}$ on the AuNPs with the state of quenched.

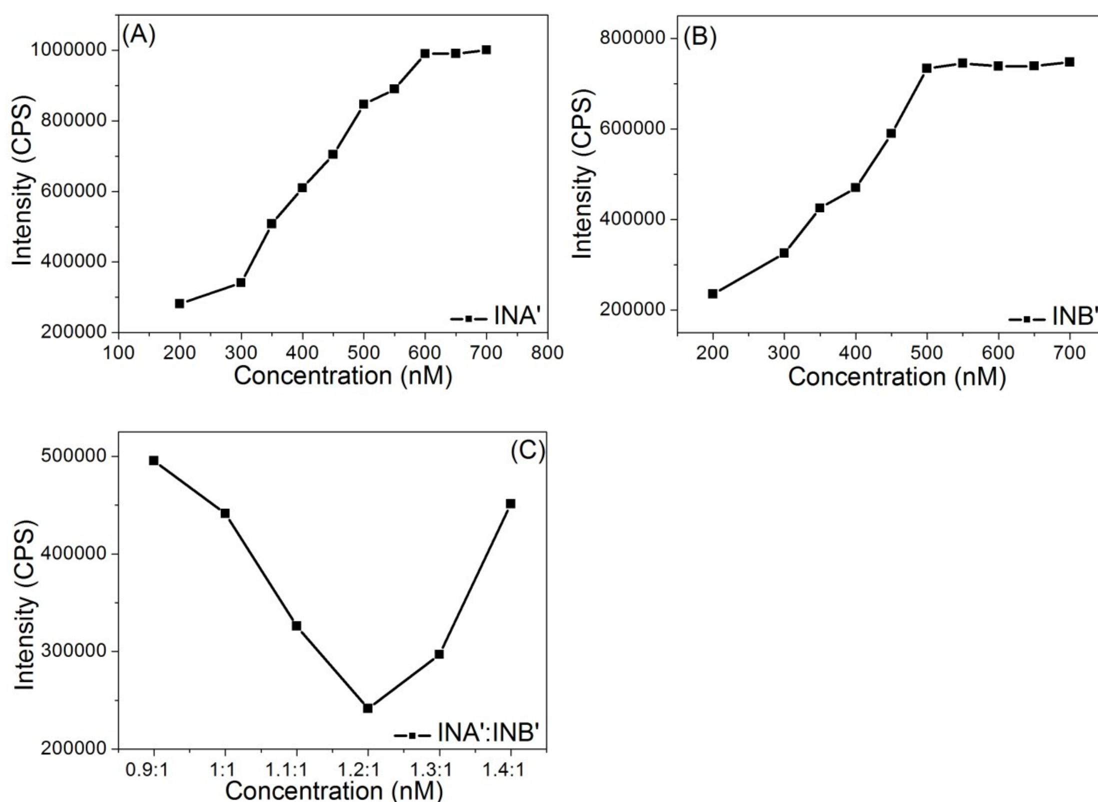


**Fig. S5** The FAM fluorescence response of AuNPs/$P_{HS}$/F-$DNA_{HS}$ complex with increasing the concentration of INA’ (A), INB’ (B) and INA’:INB’ (C).

The fluorescence of FAM is generally recovered and reaches a platum with increasing the concentration of INA’ (A), INB’ (B). The fluorescence of FAM is generally decreased when the concentration ratio is close to a proper value in (C), that is because each of the two inputs can hybridization and leave the F-$DNA_{HS}$ on the AuNPs with the state of quenched.

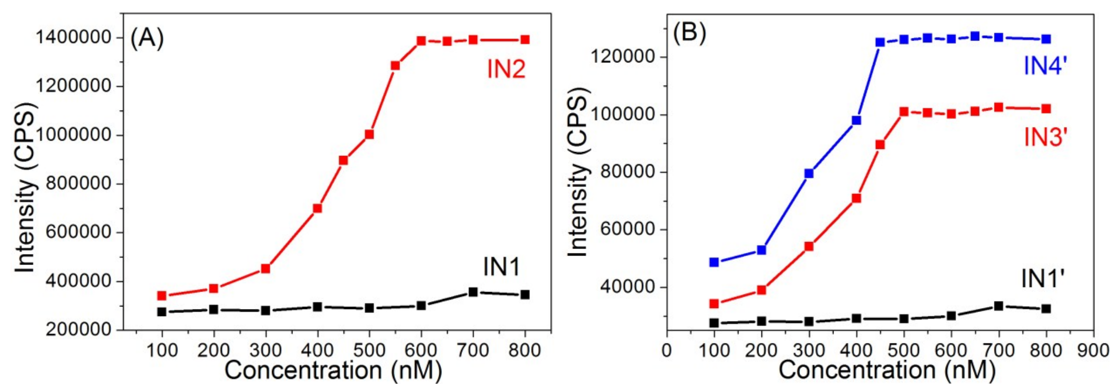


**Fig. S6** The FAM fluorescence response of (A) AuNPs/$P_{EN1}$/F-$DNA_{EN1}$ and (B) AuNPs/$P_{EN2}$/F-$DNA_{EN2}$ with increasing the concentrations of IN1 and IN2 in 2:1 encoder and IN1', IN3' and IN4' in 4:2 encoder.

The fluorescence of FAM is generally recovered and reaches a platum with increasing the concentrations of IN1 and IN2 in 2:1 encoder and IN1', IN3' and IN4' in 4:2 encoder.

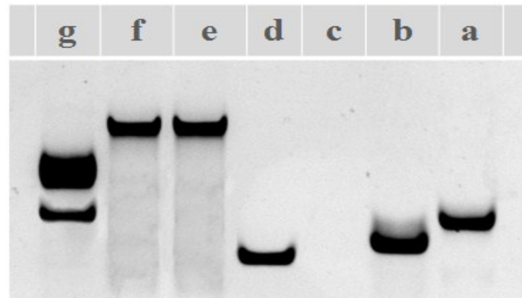


**Fig. S7** Polyacrylamide gel analysis of the 2:1 encoder logic gate. Different DNA samples were added into lanes a-g. Lane a: $P_{EN1}$; lane b: F-$DNA_{EN1}$; lane c: IN1; lane d: IN2; lane e: $P_{EN1}$+F-$DNA_{EN1}$; lane f: $P_{EN1}$+F-$DNA_{EN1}$+IN1; lane g: $P_{EN1}$+F-$DNA_{EN1}$+IN2. The concentrations for each DNA in PAGE are all 2 μM.

Native polyacrylamide gel electrophoresis (PAGE) experiments were performed to validate the hybridization reaction in 2:1 encoder logic gate. From Lane a to Lane d, they represented the DNA sequences of $P_{EN1}$, F-$DNA_{EN1}$, IN1 and IN2 as comparisons. Among them, no belt was observed from Lane c for the IN1 DNA. The possible reason might be that the IN1 was too short to stay on the gel under the experimental condition.[1] A new belt was formed in Lane e when the addition of F-$DNA_{EN1}$ into $P_{EN1}$, indicating the formation of duplex $P_{EN1}$/F-$DNA_{EN1}$. When the addition of IN1 to the mixture of $P_{EN1}$ andF-$DNA_{EN1}$, Lane f, one belt appeared at the same position as that of $P_{EN1}$/F-$DNA_{EN1}$ since the addition of IN1 did not influence the hybridization of $P_{EN1}$/F-$DNA_{EN1}$. Similar as the Lane c, the free IN1 was still not observed from the Lane f. If adding IN2 into the mixture of $P_{EN1}$ and F-$DNA_{EN1}$, two belts were monitored. One belt appeared at similar position as that of $P_{EN1}$ in Lane a. Another

one appeared at a new position, which indicated the formation of duplex of IN2/F-$DNA_{EN1}$. According to the above discussion, the PAGE results were consistent with the fluorescent results.

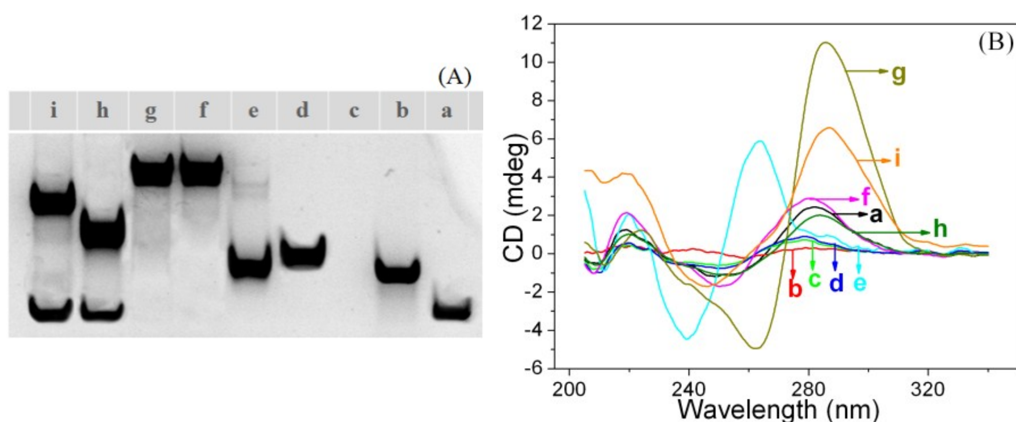


**Fig. S8** (A) Polyacrylamide gel analysis of the 4:2 encoder logic gate. Different DNA samples were added into Lanes a-i. Lane a: $P_{EN2}$; Lane b: F-$DNA_{EN2}$; Lane c: IN1'; Lane d: IN3'; Lane e: IN4'; Lane f: $P_{EN2}$+F-$DNA_{EN2}$; Lane g: $P_{EN2}$+F-$DNA_{EN2}$+IN1'; Lane h: $P_{EN2}$+F-$DNA_{EN2}$+IN3'; Lane i: $P_{EN2}$+F-$DNA_{EN2}$+IN3'. The concentrations for each DNA in PAGE are all 2 μM. (B) The circular dichroism of different DNA sequences of curve a: $P_{EN2}$; curve b: F-$DNA_{EN2}$; curve c: IN1'; curve d: IN3'; curve e: IN4'; curve f: $P_{EN2}$+F-$DNA_{EN2}$+IN1'; curve g: $P_{EN2}$+F-$DNA_{EN2}$+IN2'; curve h: $P_{EN2}$+F-$DNA_{EN2}$+IN3'; curve i: $P_{EN2}$+F-$DNA_{EN2}$+IN4' in Tris-HCl buffer (20 mM Tris-HCl, 200 mM KCl, 10 mM $MgCl_2$, pH 8.0).

We have applied PAGE and circular dichroism (CD) experiments to demonstrate the integrity of the reaction mechanism of the 4:2 encoder logic gate. The native PAGE was used to validate the hybridization of these input DNA strands in the operation of 4:2 logic gate, shown in Fig. S5A. From Lane a to Lane e represent the DNA sequences of $P_{EN2}$, F-$DNA_{EN2}$, IN1', IN3' and IN4', respectively. Similar as the PAGE results in Fig. S8A, no belt was observed for the IN1'DNA because the

sequence of IN1’ is too short to bind in the gel. Compared with the belts in Lane a and Lane b, the single belt in Lane f proved the hybridization between $P_{EN2}$ and F-$DNA_{EN2}$ and formed the duplex of $P_{EN2}$/F-$DNA_{EN2}$. The addition of IN1’ in Lane g had little effect on the stability of the $P_{EN2}$/F-$DNA_{EN2}$ duplex, which proves that no hybridization reactions happened between IN1’ and $P_{EN2}$ or between IN1’ and F-$DNA_{EN2}$. However, it is worth noting that a new belt emerged in Lane h, which can be ascribed to the formation of the IN3’/F-$DNA_{EN2}$ duplex. A new belt also emerged in Lane i since the hybridization of IN3’ with F-$DNA_{EN2}$, forming the IN3’/F-$DNA_{EN2}$ duplex.

Moreover, CD experiments were performed to identify the hybridization of DNA and formation of G-quadruplex and i-motif structure in the 4:2 encoder logic gate. The conformation of double helix, G-quadruplex and i-motif structure all own typical characteristics in the CD spectra. The CD spectrum of $P_{EN2}$, F-$DNA_{EN2}$, IN1’and IN3’ are of relatively low amplitude (curve a, b, c and d), indicating a random DNA structure. Two obvious peaks, a positive peak at 263 nm and a negative peak at 238 nm, can be found from the CD spectrum of IN4’ (curve e), which is the character of parallel G-quadruplex structure. When adding IN1’ into the complex of $P_{EN2}$/F-$DNA_{EN2}$, no obvious change is found in curve f, indicating that the addition of IN1’did not influence the hybridization between $P_{EN2}$ and F-$DNA_{EN2}$. When adding S1 into the complex of $P_{EN2}$/F-$DNA_{EN2}$, although forming the duplex of IN3’/F-$DNA_{EN2}$, no obvious change was found in curve f. The addition of $H^+$ results in the formation of i-motif configuration, curve g.[2] Once adding IN4’ into the complex of

$P_{EN2}$/F-$DNA_{EN2}$ (curve i), the number of base pairs increased with the addition of complementary sequences compared with curve e, which subsequently induced the rise of ellipticity at 286 nm and the drop at 245 nm, indicating that the hybridization between IN4' and F-$DNA_{EN2}$ happened with the G-quadruplex configuration. Both PAGE and CD results further demonstrate DNA interactions and the formation of G-quadruplex and i-motif occur as the expected way for the feasibility of the 4:2 encoder logic gate.

## References


1 Y. Jiang, B. L. Li, X. Chen, A. D. Ellington, *Molecules* 2012, **17**, 13211-13220.

2 X. Zhang, M. R. Servos, J. W. Liu, *J. Am. Chem. Soc.* 2012, **134**, 7266-7269.