SUPPORTING INFORMATION

DNA Template-Regulated Intergrowth of Fluorescent Silver Nanocluster Emitter Pair

Jin-Liang Ma, Bin-Cheng Yin, and Bang-Ce Ye**

Lab of Biosystem and Microanalysis, State Key Laboratory of Bioreactor Engineering, East China University of Science & Technology, Shanghai, 200237, P. R. China

Corresponding author: Bin-Cheng Yin, binchengyin@ecust.edu.cn; Bang-Ce Ye, bcye@ecust.edu.cn.

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1. The Information of Oligonucleotides Used in This Study

Table S1. Sequence information for oligonucleotides used in this study

No.	Name	Sequence* (5'-3')
1	T1	T_{15}-CCCTAACTCCCC
2	T2	CCCTTAATCCCC-A_{15}
3	T3	TATATATATTTCCCTTAATCCCCAACTATACAACCTACTA
4	T4	TAGTAGGTTGTATAGTTCCCTAACTCCCCAAATATATATA
5	T5	CCCTTAATCCCCTGAGGTAGTAACTATACAACCTACTACCTCACCCTAACTCCCC
6	T6	TAGTAGGTTGTATAGTTCCCTTAATCCCCTCCCTAACTCCCCAACTATACAACCTACTA
7	S-T_{70}	CCCTTAATCCCC-T_{70}-CCCTAACTCCCC
8	S-T_{35}	CCCTTAATCCCC-T_{35}-CCTAACTCCCC
9	S-T_{30}	CCCTTAATCCCC-T_{30}-CCCTAACTCCCC
10	S-T_{25}	CCCTTAATCCCC-T_{25}-CCCTAACTCCCC
11	S-T_{20}	CCCTTAATCCCC-T_{20}-CCCTAACTCCCC
12	S-T_{15}(YN)	CCCTTAATCCCC-T_{15}-CCCTAACTCCCC
13	S-T_{10}	CCCTTAATCCCC-T_{10}-CCCTAACTCCCC
14	S-T_5	CCCTTAATCCCC-T_5-CCCTAACTCCCC
15	S-A_{35}	CCCTTAATCCCC-A_{35}-CCCTAACTCCCC
16	S-A_{30}	CCCTTAATCCCC-A_{30}-CCCTAACTCCCC
17	S-A_{25}	CCCTTAATCCCC-A_{25}-CCCTAACTCCCC
18	S-A_{20}	CCCTTAATCCCC-A_{20}-CCCTAACTCCCC
19	S-A_{15}	CCCTTAATCCCC-A_{15}-CCCTAACTCCCC
20	S-A_{10}	CCCTTAATCCCC-A_{10}-CCCTAACTCCCC
21	S-A_5	CCCTTAATCCCC-A_5-CCCTAACTCCCC
22	S-C_{35}	CCCTTAATCCCC-C_{35}-CCCTAACTCCCC
23	S-C_{30}	CCCTTAATCCCC-C_{30}-CCCTAACTCCCC
24	S-C_{25}	CCCTTAATCCCC-C_{25}-CCCTAACTCCCC
25	S-C_{20}	CCCTTAATCCCC-C_{20}-CCCTAACTCCCC

26	**S-C_{15}**	CCCTTAATCCCC-C_{15}-CCCTAACTCCCC
27	**S-C_{10}**	CCCTTAATCCCC-C_{10}-CCCTAACTCCCC
28	**S-C_5**	CCCTTAATCCCC-C_5-CCCTAACTCCCC
29	**S-0**	CCCTTAATCCCCCCCTAACTCCCC
30	**S-G_1**	CCCTTAATCCCCGCCCTAACTCCCC
31	**S-G_3**	CCCTTAATCCCCGGGCCCTAACTCCCC
32	**S-G_7**	CCCTTAATCCCCGGTTGGGCCCTAACTCCCC
33	**S-G_8**	CCCTTAATCCCCGGGGTGGGCCCTAACTCCCC
34	**S-G_{13}**	CCCTTAATCCCCGGGGTGGGGTGGGCCCTAACTCCCC
35	**S-G_{16}**	CCCTTAATCCCCGGTGGGGTGGGGTGGGCCCTAACTCCCC
36	**S-G_{18}**	CCCTTAATCCCCGGGGTGGGGTGGGGTGGGCCCTAACTCCCC
37	**S-AT**	CCCTTAATCCCCTTTTATATATTATATCCCTAACTCCCC
38	**C-AT**	ATATAATATATAAAA
39	**T7**	CCCTTAATCCCCAACTATACAACCTACTACCTCA
40	**T8**	TAGTAGGTTGTATAGTTCCCTAACTCCCC
41	**I**	TGAGGTAGTAGGTTGTATAGTT
42	**S-R_{15}-C_0**	CCCTTAATCCCCTTATATAATTTATTACCCTAACTCCCC
43	**S- R_{15}-C_3**	CCCTTAATCCCCCTATACAATTTACTACCCTAACTCCCC
44	**S- R_{15}-C_4**	CCCTTAATCCCCCTATACAATCTACTACCCTAACTCCCC
45	**S-R_{15}-C_5**	CCCTTAATCCCCCTATACAACCTACTACCCTAACTCCCC
46	**S- R_{22}-C_0**	CCCTTAATCCCCAATTATATAATTTATTATTTTACCCTAACTCCCC
47	**S-R_{22}-C_6**	CCCTTAATCCCCAACTATACAATCTACTACTTCACCCTAACTCCCC
48	**S-R_{22}-C_8**	CCCTTAATCCCCAACTATACAACCTACTACCTCACCCTAACTCCCC
49	**S-PEG_5-T_4**	CCCTTAATCCCCTT-CH_2-(CH_2-O-CH_2)$_5$-CH_2-TTCCCTAACTCCCC
50	**S-PEG_5**	CCCTTAATCCCC-CH_2-(CH_2-O-CH_2)$_5$-CH_2-CCCTAACTCCCC
51	**BG**	CCCTTTAACCCC -T_{15}-CCCTCTTAACCC
52	**BY**	CCCTTTAACCCC-T_{15}-CCCTTAATCCCC
53	**BR**	CCCTTTAACCCC-T_{15}-CCTCCTTCCTCC
54	**BN**	CCCTTTAACCCC-T_{15}-CCCTAACTCCCC
55	**GY**	CCCTCTTAACCC-T_{15}-CCCTTAATCCCC

56	**GR**	**CCCTCTTAACCC**-T_{15}-**CCTCCTTCCTCC**
57	**GN**	**CCCTCTTAACCC**-T_{15}-**CCCTAACTCCCC**
58	**YR**	**CCCTTAATCCCC**-T_{15}-**CCTCCTTCCTCC**
59	**RN**	**CCTCCTTCCTCC**-T_{15}-**CCCTAACTCCCC**
60	**YY**	**CCCTTAATCCCC**-T_{15}-**CCCCTAATTCCC**
61	**NN**	**CCCCTCAATCCC**-T_{15}-**CCCTAACTCCCC**
62	**BB**	**CCCTTTAACCCC**-T_{15}-**CCCCAATTTCCC**
63	**GG**	**CCCAATTCTCCC**-T_{15}-**CCCTCTTAACCC**
64	**RR**	**CCTCCTTCCTCC**-T_{15}-**TCCTCCTTCCTCC**
65	**T_{15}-N**	T_{15}- **CCCCTCAATCCC**
66	**N-T_{15}**	**CCCCTCAATCCC**-T_{15}
67	**Y-T_{15}**	**CCCTTAATCCCC**-T_{15}
68	**R-T_{15}**	**CCTCCTTCCTCC**-T_{15}
69	**G-T_{15}**	**CCCTCTTAACCC**-T_{15}
70	**B-T_{15}**	**CCCTTTAACCCC**-T_{15}
71	**S-1**	**CCCTTAATCCCC**TATAATAAATTTTAAATATTATTTATTAAT
72	**S-G**	ATTAATAAATAATATTTAAAATTTATTATA**GGGTGGGGTGGGGTGGGG**
73	**Y**	**CCCTTAATCCCC**
74	**N**	**CCCTAACTCCCC**

*The nucleobases in orange, purple, blue, green and red color represent yellow, near-IR, blue, green and red emitter-nucleation sequences, respectively. The nucleobases in wine red represent G-enhancer sequences.

2. Supplementary Results

2.1 Four modes of emitter pair

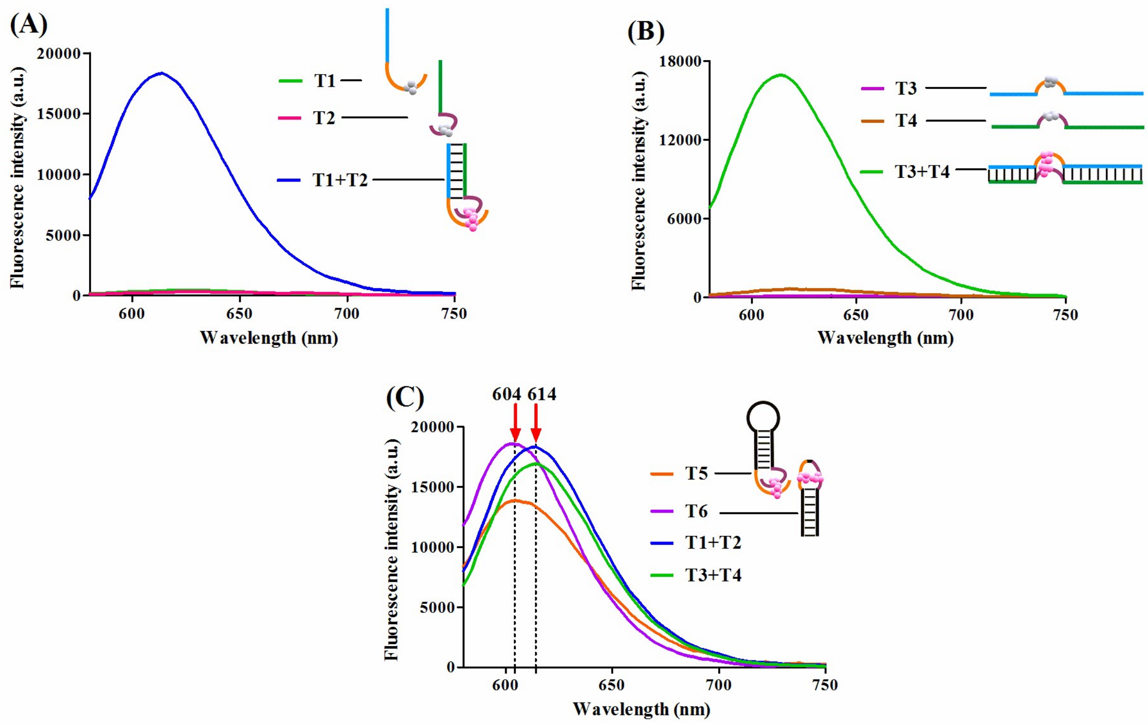

Figure S1. Fluorescence emission spectra of four modes of emitter pair in close proximity. (A) Emission spectra of DNA/AgNCs produced by T1, T2, and the mixture of T1 and T2, respectively. The produced emitter pairs are located at end of T1 and T2 with complementary tails of polythymine and polyadenine, which are difficult to binding Ag ions, exclude the possibility that complementary stem domain participates to form fluorescent emitter pair. (B) Emission spectra of DNA/AgNCs produced by T3, T4, and the mixture of T3 and T4, respectively. (C) Comparison of fluorescence emission of DNA/AgNCs stabilized by four modes of emitter pairs provided by T5, T6, mixture of T1 and T2, and mixture of T3 and T4. The final concentrations of all DNA templates used in the reaction system were 1 μM.

2.2 S-T_n/AgNC (n=5, 10, 15, 20, 25, 30, 35, 70), S-0/AgNC, Y-T_{15}/AgNCs, and T_{15}-N/AgNCs

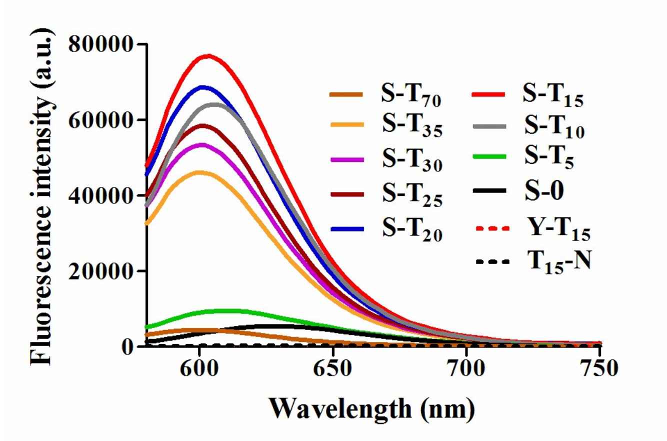

Figure S2. Fluorescence emission spectra of AgNCs stabilized by S-T_n (n=5, 10, 15, 20, 25, 30, 35, 70**)** with n thymines, S-0 without spacer, Y-T_{15} containing Y emitter and 15-nt polythymine spacer and T_{15}-N containing N emitter and 15-nt polythymine spacer.

2.3 S-G_n/AgNCs (n=1, 3, 5, 7, 10, 16 and 18)

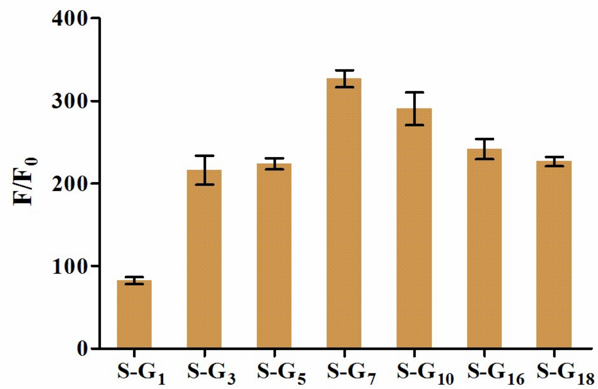

Figure S3. The fluorescence enhancement ratio F/F_0 values for AgNCs stabilized by DNA template (S-G_n, n=1, 3, 5, 7, 10, 16 and 18) with guanine-rich spacers. F is the fluorescence intensity of S-G_n/AgNCs at 646 nm, F_0 is the fluorescence intensity of Y-T_{15}/AgNCs at 646 nm. The reason of selection of guanine-rich sequence not polyguanine is that longer polyguanine sequence cannot be obtained by the limited commercial DNA synthesis technology. The final concentrations of all DNA templates used in the reaction system were 1 μM.

2.4 Changes in fluorescence intensity before and after adding inhibitor

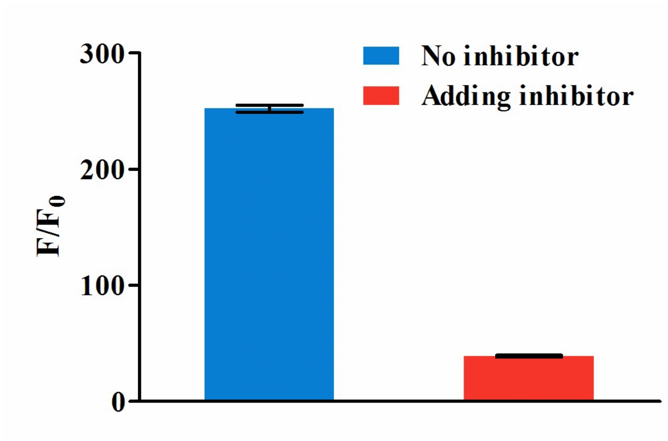

Figure S4. Comparison in the fluorescence intensity of S-AT/AgNCs before and after adding the complement of spacer in S-AT as inhibitor. F is the fluorescence intensities of AgNCs stabilized by S-AT at 608 nm, F_0 is the fluorescence intensities of Y-T_{15}/AgNCs at 608 nm.

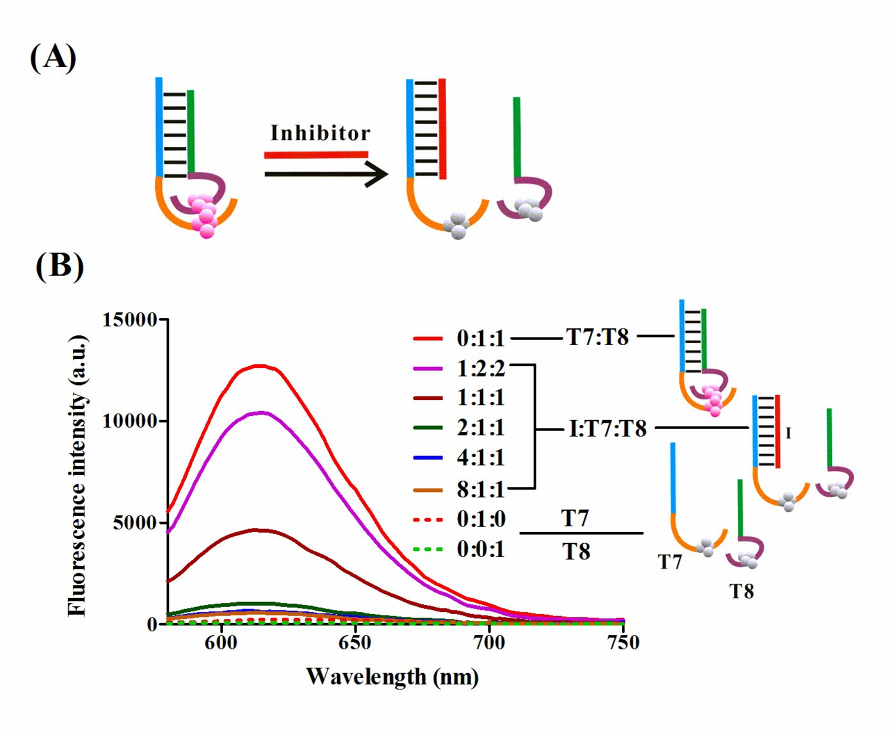

Figure S5. (A) Schematic illustration of the fluorescence quenching of Ag emitter pair from the duplex of T7 and T8 via the hybridization between T7 and inhibitor. (B) Emission spectra of DNA/AgNCs produced by the mixture of T7, T8, and inhibitor (I) according to different molar ratios (I/T7/T8 ratios).

In the competitive binding experiment, the molar ratio [0:1:1] indicates the mixture of 0 μM I, 1 μM T7 and 1 μM T8, [0:1:0] and [0:0:1] indicate 1 μM T7 and 1 μM T8 present alone, respectively; [1:2:2], [1:1:1], [2:1:1], [4:1:1], and [8:1:1] indicate 0.5 μM, 1 μM, 2 μM, 4 μM and 8 μM I plus 1 μM T7 and 1 μM T8, respectively.

2.5 The replacement of nucleobase in spacer of DNA template

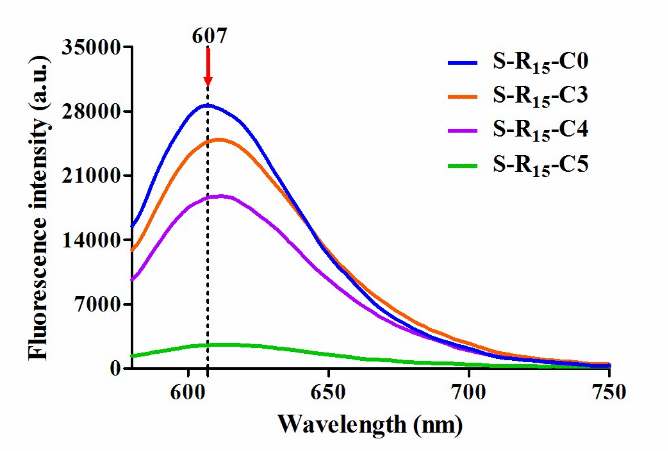

Figure S6. Comparison of fluorescence emission spectra of AgNCs stabilized by DNA templates containing increased number of cytosines in a spacer sequence initially containing only adenine and thymine. S-R_{15}-C_3, S-R_{15}-C_4, and S-R_{15}-C_5 represent the DNA templates with substitution of 3 thymines, 4 thymines, and 5 thymines by cytosine in the original 15-nt adenine- and thymine-rich spacer sequence, respectively, and the DNA template (S-R_{15}-C_0) without cytosine in spacer sequence as a control. The final concentrations of tested DNA templates in the reaction system were 1 μM.

2.6 S-PEG(5)-T4/AgNCs and S-PEG(5)/AgNCs

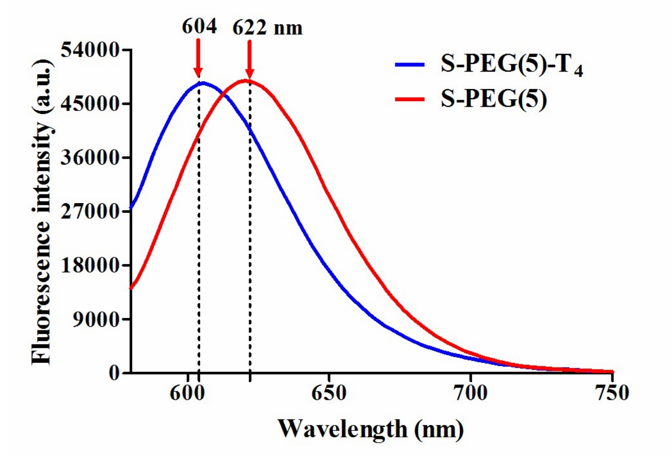

Figure S7. Fluorescence emission spectra of AgNCs stabilized by S-PEG(5)-T4 containing uncharged poly-ethylene glycol (PEG) and 4-nt thymines and S-PEG(5) without 4-nt thymines, respectively. The final concentrations of all the templates in the reaction system were 1 μM.

2.7 The emission spectra of DNA/AgNCs at different excitation

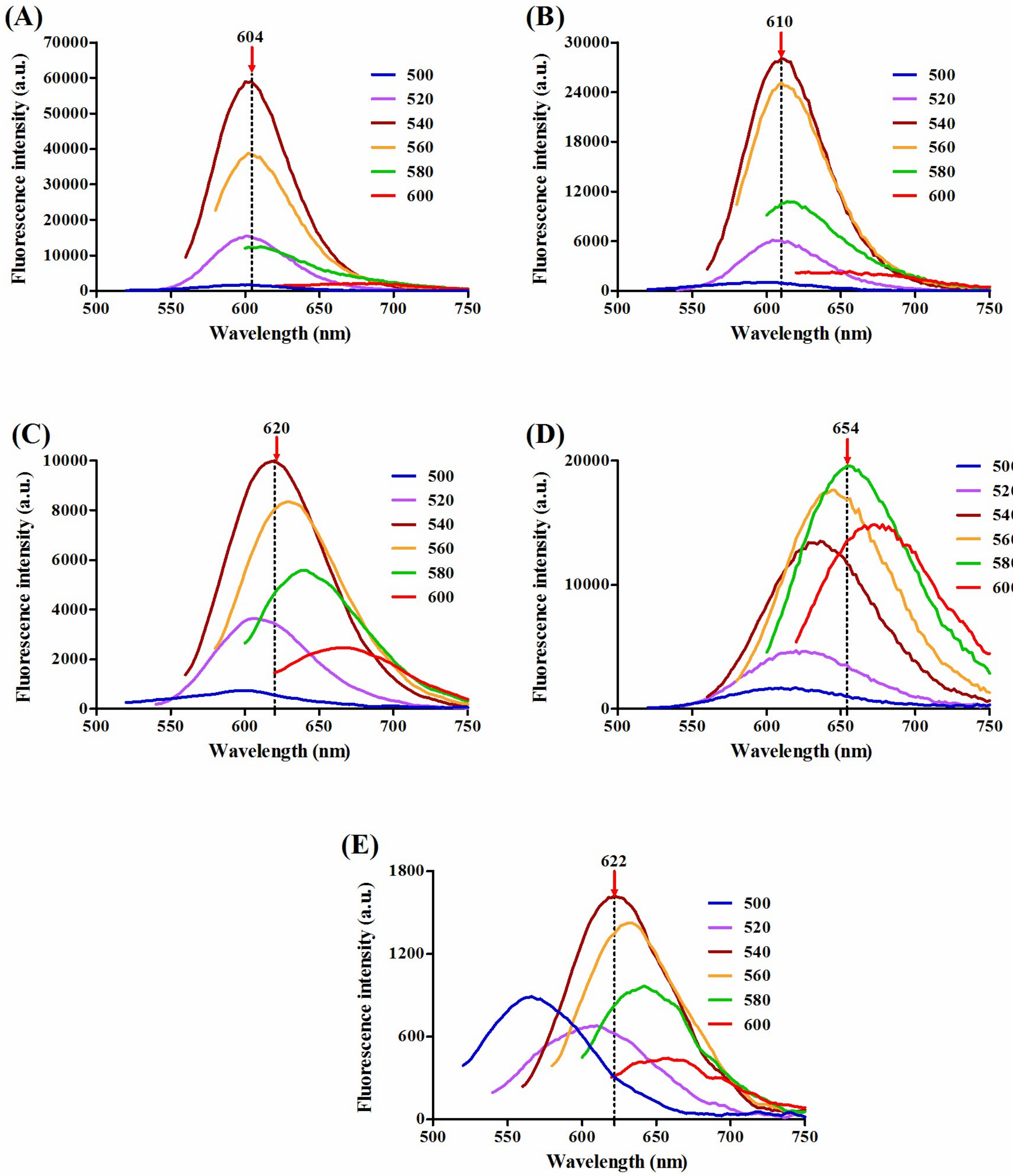

Figure S8. Fluorescence emission spectra of AgNCs stabilized by (A) S-T_{15}, (B) S-A_{15}, (C) S-C_{15}, (D) S-G_{16}, and (E) S-0, respectively, with excitation from 500-600 nm in 20 nm steps.

2.8 The mixture of two templates containing one emitter and 15-nt polythymine

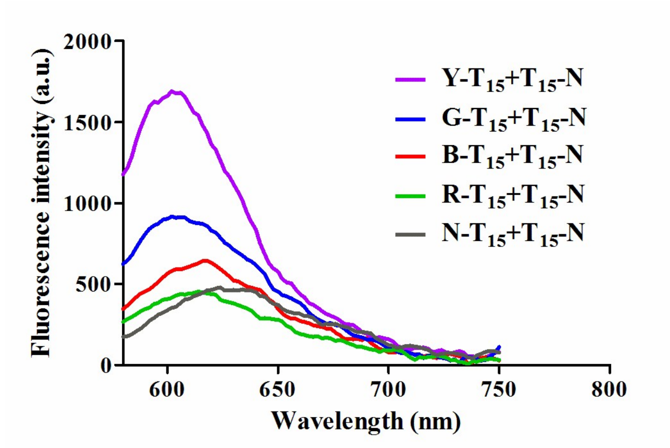

Figure S9. Fluorescence emission spectra of AgNCs stabilized by mixture of the two DNA templates containing one emitter-nucleation sequence and 15-nt polythymine spacer. The final concentrations of all DNA templates in the reaction system were 1 μM.

2.9 Comparison of DNA/AgNCs from our design and the reported templates.

Table S2. Comparison of DNA/AgNCs from our design and the reported templates.

DNA template	Concentration (μM)	Reduction time (min)	Excitation/Emission (nm)	Fluorescence intensity (a.u.)
S-T_{15}	1	15	550/604	60239±288
S-1 and S-G[1]	1	60	568/630	35934±942
Y[2]	1	60	472/562	544±3
N[2]	1	60	560/616	1460±49

2.10 The investigation on energy transfer

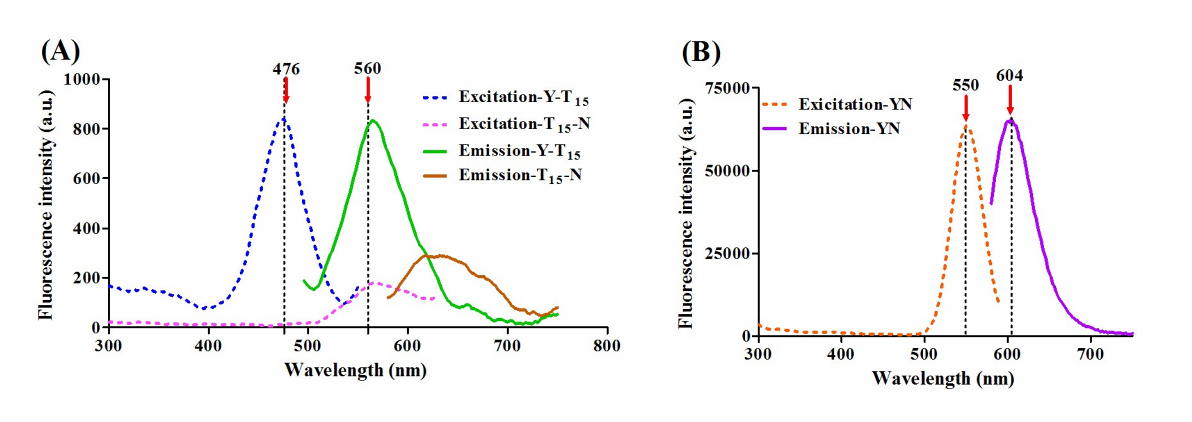

Figure S10. (A) Excitation (dashed curves) and emission spectra (solid curves) for Y-T_{15} and T_{15}-N. Y-T_{15} contains with a yellow emitter and 15-nt polythymine spacer, and T_{15}-N contains a near-IR emitter and 15-nt polythymine spacer. The final concentrations of Y-T_{15} and T_{15}-N templates were 1 μM in the reaction system. (B) Excitation (dashed curves) and emission spectra (solid curves) for YN template (equal to S-T_{15}). The final concentrations of the templates in the reaction system were 1 μM.

2.11 The effect of $AgNO_3$ with different concentration

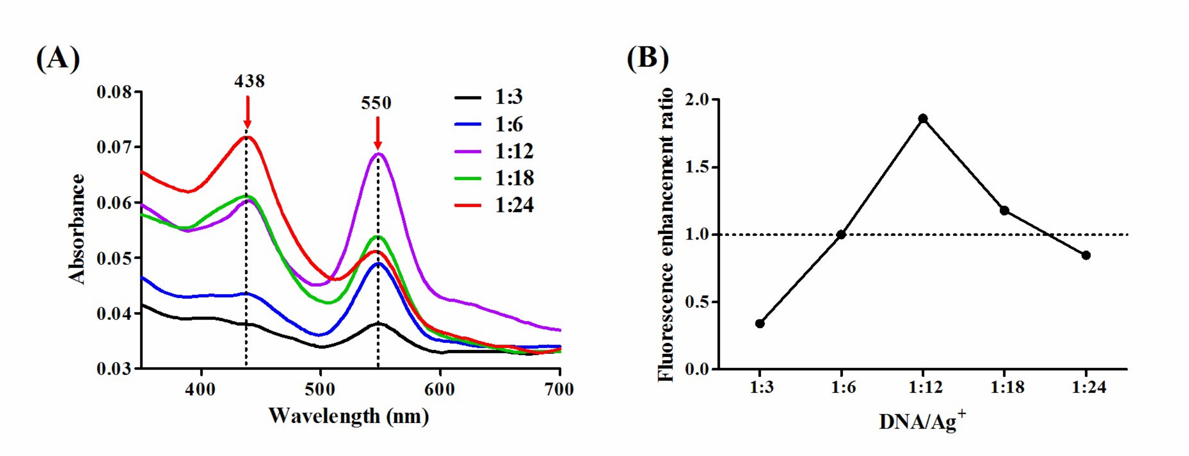

Figure S11. (A) Absorption spectra of AgNCs stabilized by S-T_{15} after adding $AgNO_3$ with different concentration. (B) The fluorescence enhancement ratio change with increase of $AgNO_3$. The fluorescence enhancement ratio is the fluorescence intensity of DNA/AgNCs at 604 nm under different ratio of DNA/Ag^+ versus the fluorescence intensity of DNA/AgNCs with 1:6 of DNA/Ag^+ at 604 nm used in the conventional method.

2.12 The effect of different pH

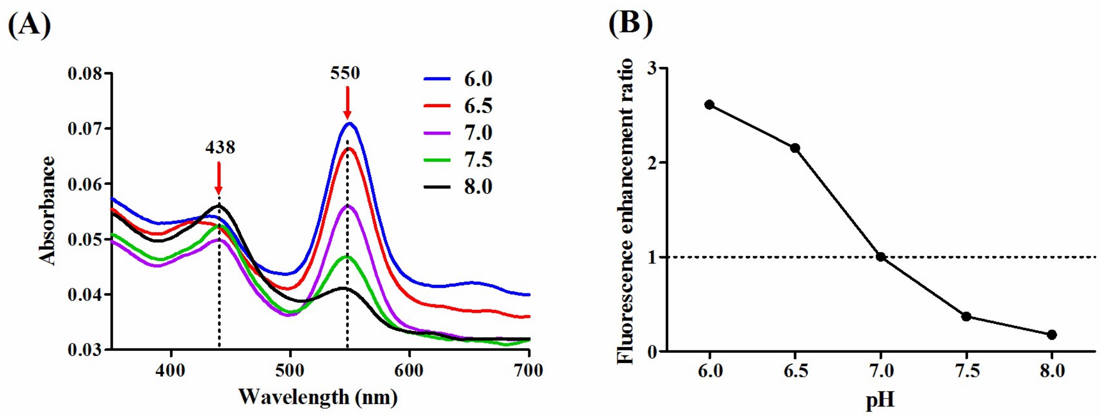

Figure S12. (A) Absorption spectra of AgNCs stabilized by S-T_{15} at different pH. (B) The fluorescence enhancement ratio change with pH from 6.0 to 8.0. The fluorescence enhancement ratio is the fluorescence intensity of DNA/AgNCs at different pH versus the fluorescence intensity of DNA/AgNCs under pH 7.0 at 604 nm used in the conventional method.

3. References

1 H. C. Yeh, J. Sharma, J. J. Han, J. S. Martinez and J. H. Werner, *Nano Lett.*, 2010, **10**, 3106-3110.

2 C. I. Richards, S. Choi, J. C. Hsiang, Y. Antoku, T. Vosch, A. Bongiorno, Y. L. Tzeng and R. M. Dickson, *J. Am. Chem. Soc.*, 2008, **130**, 5038-5039.