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Electronic Supplementary Information

dsDNA-templated fluorescent copper nanoparticles: poly(AT-TA)-dependent formation

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Chemicals and materials

The oligonucleotides ds(G-C)$_{22}$ of HPLC grade were synthesized and purified by Takara Biotechnology Co., Ltd. (Dalian, China), other oligonucleotides of HPLC grade were synthesized and purified by Shanghai Sangon Biological Engineering Technology and Services Co., Ltd. (Shanghai, China). The sequences of oligonucleotides used for each figure are listed in Table S1 to Table S5, respectively. All oligonucleotides were dissolved in sterile ultrapure water; each oligonucleotide of 10 μM was prepared as its stock solution. 3-(N-morpholino) propanesulfonic acid (MOPS), sodium ascorbate, copper sulfate and other salt reagents were commercially obtained from Dingguo Biotechnology Co., Ltd. (Beijing, China). All salts used in this work were of analytical grade at least and used without further treatment. MOPS buffer (10 mM MOPS, 150 mM NaCl, pH 7.8) was used for the synthesis of dsDNA-templated fluorescent CuNPs. Ultrapure water was prepared by the Nanopure Infinity™ ultrapure water system (Barnstead/Thermolyne Corp.).

Measurements

Fluorescence measurements, including fluorescence spectra, fluorescence intensity, 3D scan, and real-time fluorescence monitoring, were carried out on an F-7000 fluorescence spectrophotometer (Hitachi, Japan). The Ex and Em slits of the spectrophotometer were set at 5.0 and 10.0 nm, respectively, with a 700 V PMT voltage and a 0.2 s response time. Excitation wavelength was set at 340 nm, and fluorescence emission spectra were obtained by collecting emission intensity from 500 to 660 nm with a 0.2 cm × 1 cm quartz cuvette containing 100 μL solution. UV-

visible absorption measurements were recorded using a UV-2600 spectrophotometer (Shimadzu, Japan). The fluorescence emission images of CuNPs were recorded by a digital camera from a WD-9403 imaging system (Shanghai, China) with a transmitted ultraviolet light. Transmission electron microscopy (TEM) measurements were performed on a JEM-3010 transmission electron microscope (JEOL, Japan) operated at 300 kV. The temperature for all measurements was controlled by an aqueous thermostat (Amersham) which is accurate to 0.1 °C, all measurements were carried out at room temperature (20 °C) unless stated otherwise.

Preparation of dsDNA-templated fluorescent CuNPs

Firstly, 200 nM dsDNA was mixed in MOPS buffer (10 mM MOPS, 150 mM NaCl, pH 7.8). The mixture was incubated at room temperature (20 °C) for 5 min to ensure that the two strands of dsDNA hybridized with each other completely. Then 1 mM ascorbic acid and 100 μM $CuSO_4$ was added and triggered the formation reaction of fluorescent CuNPs. After another incubation of 10 min, 100 μL of the resulted solution was added into the quartz cuvette for the fluorescence measurement.

Table S1 dsDNA sequences used for Fig. 2, Fig. S1, Fig. S2, and Fig. S3.

name	sequence	length
ds(AT-TA)$_{22}$	5′-ATATATATATATATATATATAT-3′ 3′-TATATATATATATATATATATA-5′	22 bp
ds(GC-CG)$_{22}$	5′-GCGCGCGCGCGCGCGCGCGCGC-3′ 3′-CGCGCGCGCGCGCGCGCGCGCG-5′	22 bp
ds(AG-TC)$_{22}$	5′-AGAGAGAGAGAGAGAGAGAGAG-3′ 3′-TCTCTCTCTCTCTCTCTCTCTC-5′	22 bp
ds(AC-TG)$_{22}$	5′-ACACACACACACACACACACAC-3′ 3′-TGTGTGTGTGTGTGTGTGTGTG-5′	22 bp
ds(A-T)$_{22}$	5′-AAAAAAAAAAAAAAAAAAAAAA-3′ 3′-TTTTTTTTTTTTTTTTTTTTTT-5′	22 bp
ds(G-C)$_{22}$	5′-GGGGGGGGGGGGGGGGGGGGGG-3′ 3′-CCCCCCCCCCCCCCCCCCCCCC-5′	22 bp
ds(R-R)$_{22}$	5′-CTCATACGTTCATCACGACTAC-3′ 3′-GAGTATGCAAGTAGTGCTGATG-5′	22 bp

Table S2 dsDNA sequences used for figure 3 and Fig. S4

name	sequence	length
ds(AT-TA)$_{22}$	5′-ATATATATATATATATATATAT-3′ 3′-TATATATATATATATATATATA-5′	22 bp
ds(A_2T_2-T_2A_2)$_{22}$	5′-AATTAATTAATTAATTAATTAA-3′ 3′-TTAATTAATTAATTAATTAATT-5′	22 bp
ds(A_3T_3-T_3A_3)$_{22}$	5′-AAATTTAAATTTAAATTTAAAT-3′ 3′-TTTAAATTTAAATTTAAATTTA-5′	22 bp
ds(A_4T_4-T_4A_4)$_{22}$	5′-AAAATTTTAAAATTTTAAAATT-3′ 3′-TTTTAAAATTTTAAAATTTTAA-5′	22 bp
ds(A_5T_5-T_5A_5)$_{22}$	5′-AAAAATTTTTAAAAATTTTTAA-3′ 3′-TTTTTAAAAATTTTTAAAAATT-5′	22 bp
ds(A_6T_6-T_6A_6)$_{22}$	5′-AAAAAATTTTTT AAAAAATTTT-3′ 3′-TTTTTTAAAAAATTTTTTAAAA-5′	22 bp
ds($A_{11}T_{11}$-$T_{11}A_{11}$)$_{22}$	5′-AAAAAAAAAAATTTTTTTTTTT-3′ 3′-TTTTTTTTTTTAAAAAAAAAAA-5′	22 bp

Table S3 dsDNA sequences used for Fig. 4 and Fig. S5

name	sequence	length
ds(ATGC-TACG)$_{44}$	5′-ATGCATGCATGCATGCATGCATGCATGCATGCATGC-3′ 3′-TACGTACGTACGTACGTACGTACGTACGTACGTACG-5′	44 bp
ds(AT-TA)$_{11}$(GC-CG)$_{11}$(AT-TA)$_{11}$(GC-CG)$_{11}$	5′-ATATATATATAGCGCGCGCGTATATATATATCGCGCGCGCGC-3′ 3′-TATATATATATCGCGCGCGCATATATATATAGCGCGCGCGCG-5′	44 bp
ds(AT-TA)$_{14}$(GC-CG)$_{11}$(AT-TA)$_{8}$(GC-CG)$_{11}$	5′-ATATATATATATATGCGCGCGCGATATATATCGCGCGCGCGC-3′ 3′-TATATATATATATACGCGCGCGCGCTATATATAGCGCGCGCGCG-5′	44 bp
ds(AT-TA)$_{18}$(GC-CG)$_{11}$(AT-TA)$_{4}$(GC-CG)$_{11}$	5′-ATATATATATATATATATGCGCGCGCGCGATATCGCGCGCGCGC-3′ 3′-TATATATATATATATATACGCGCGCGCGCTATAGCGCGCGCGCG-5′	44 bp
ds(AT-TA)$_{22}$(GC-CG)$_{22}$	5′-ATATATATATATATATATATATATGCGCGCGCGCGCGCGCGCGC-3′ 3′-TATATATATATATATATATATATACGCGCGCGCGCGCGCGCGCG-5′	44 bp

Table S4 dsDNA sequences used for Fig. 5 and Fig. S6

name	sequence	length
ds(AT-TA)$_{14}$	5′-ATATATATATATAT-3′ 3′-TATATATATATATA-5′	14 bp
ds(AT-TA)$_{18}$	5′-ATATATATATATATATAT-3′ 3′-TATATATATATATATATA-5′	18 bp
ds(AT-TA)$_{22}$	5′-ATATATATATATATATATATAT-3′ 3′-TATATATATATATATATATATA-5′	22 bp
ds(AT-TA)$_{26}$	5′-ATATATATATATATATATATATATAT-3′ 3′-TATATATATATATATATATATATATA-5′	26 bp

ds(AT-TA)$_{30}$	5′-ATATATATATATATATATATATATATATAT-3′ 3′-TATATATATATATATATATATATATATATA-5′	30 bp

Table S5 dsDNA sequences used for Fig. S7

name	**sequence**	**length**
ds(AT-TA)$_{22}$	5′-ATATATATATATATATATATAT-3′ 3′-TATATATATATATATATATATA-5′	22 bp
ds(GC-CG)$_2$(AT-TA)$_{18}$(GC-CG)$_2$	5′-GCATATATATATATATATATGC-3′ 3′-CGTATATATATATATATATACG-5′	22 bp
ds(GC-CG)$_4$(AT-TA)$_{14}$(GC-CG)$_4$	5′-GCGCATATATATATATATGCGC-3′ 3′-CGCGTATATATATATATACGCG-5′	22 bp
ds(GC-CG)$_6$(AT-TA)$_{10}$(GC-CG)$_6$	5′-GCGCGCATATATATATGCGCGC-3′ 3′-CGCGCGTATATATATACGCGCG-5′	22 bp
ds(GC-CG)$_8$(AT-TA)$_6$(GC-CG)$_8$	5′-GCGCGCGCATATATGCGCGCGC-3′ 3′-CGCGCGCGTATATACGCGCGCG-5′	22 bp
ds(GC-CG)$_{10}$(AT-TA)$_2$(GC-CG)$_{10}$	5′-GCGCGCGCGCATGCGCGCGCGC-3′ 3′-CGCGCGCGCGTACGCGCGCGCG-5′	22 bp
ds(GC-CG)$_{22}$	5′-GCGCGCGCGCGCGCGCGCGCGC-3′ 3′-CGCGCGCGCGCGCGCGCGCGCG-5′	22 bp

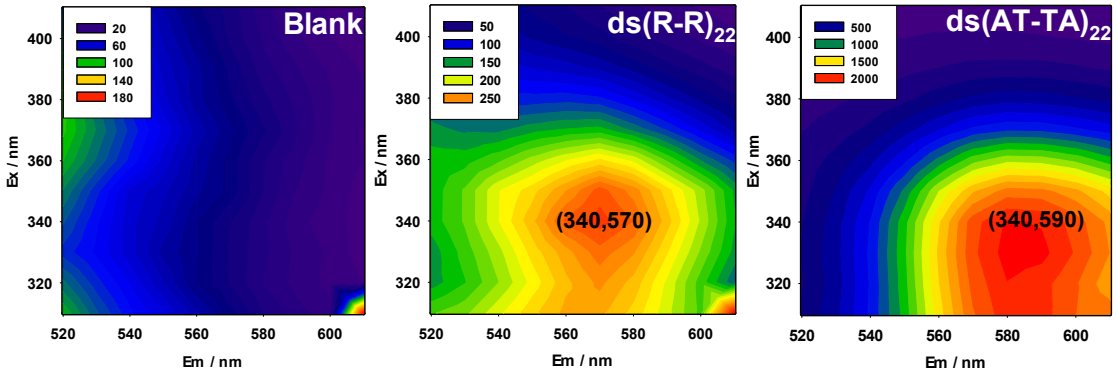

Fig. S1 3D scan of the CuNPs templated by different dsDNA in MOPS buffer (10 mM MOPS, 150 mM NaCl, pH 7.8) in the presence of 1 mM ascorbic acid and 100 μM $CuSO_4$. Detailed sequence information of each dsDNA used here is listed in the Table S1.

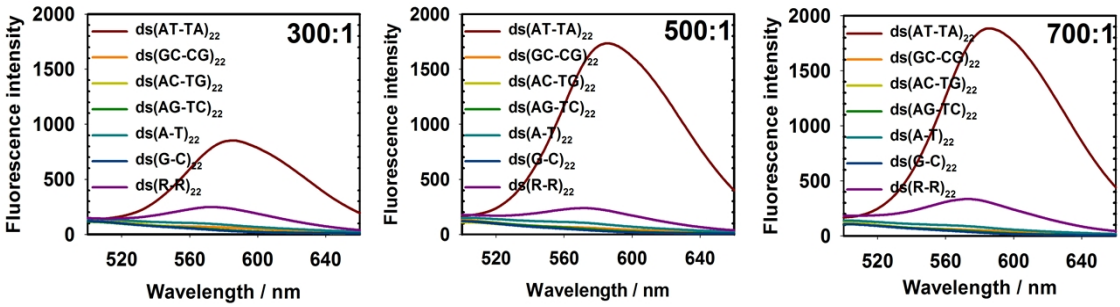

Fig. S2 The sequence selectivity at different concentration ratios of $CuSO_4$ and DNA. (from 300:1 to 700:1 for $[Cu^{2+}]$:[DNA]). Detailed sequence information of each dsDNA used here is listed in the Table S1.

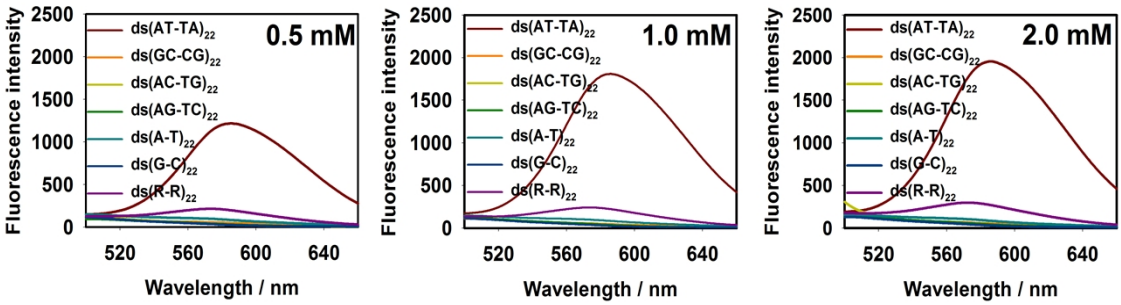

Fig. S3 The sequence selectivity at different concentration of ascorbic acid (from 0.5 mM to 2 mM). Detailed sequence information of each dsDNA used here is listed in the Table S1.

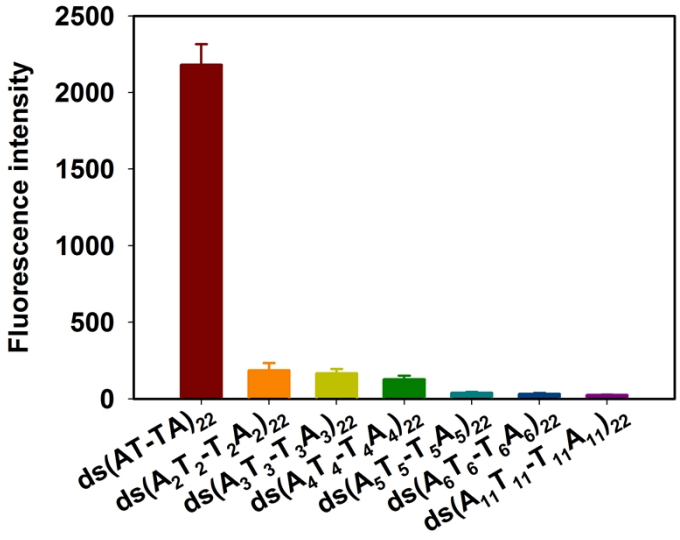

Fig. S4 Fluorescence intensity of fluorescent CuNPs templated by 22-bp dsDNA with different repetitive type of A plus T. The error bars represent the standard deviation of three independent measurements. Detailed sequence information of each dsDNA used here is listed in the Table S2.

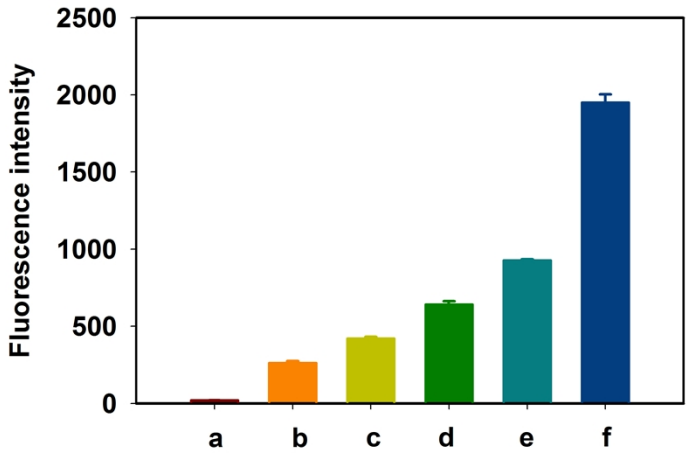

Fig. S5 Fluorescence intensity of fluorescent CuNPs templated by 44-bp dsDNA containing different (AT-TA)-rich domains. The error bars represent the standard deviation of three independent measurements. **a**, blank; **b**, ds(ATGC-TACG)$_{44}$; **c**, ds(AT-TA)$_{11}$(GC-CG)$_{11}$(AT-TA)$_{11}$(GC-CG)$_{11}$; **d**, ds(AT-TA)$_{14}$(GC-CG)$_{11}$(AT-TA)$_{8}$(GC-CG)$_{11}$; **e**, ds(AT-TA)$_{18}$(GC-CG)$_{11}$(AT- TA)$_{4}$(GC-CG)$_{11}$; **f**, ds(AT-TA)$_{22}$(GC-CG)$_{22}$. Detailed sequence information of each dsDNA used here is listed in the Table S3.

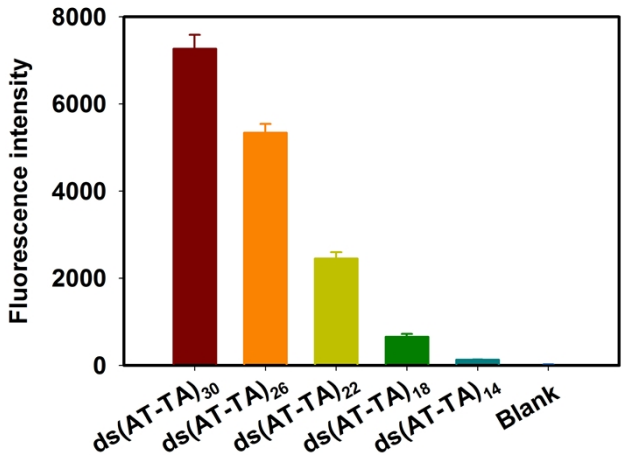

Fig. S6 Fluorescence intensity of fluorescent CuNPs templated by poly(AT-TA) DNA of different length. The error bars represent the standard deviation of three independent measurements. Detailed sequence information of each dsDNA used here is listed in the Table S4.

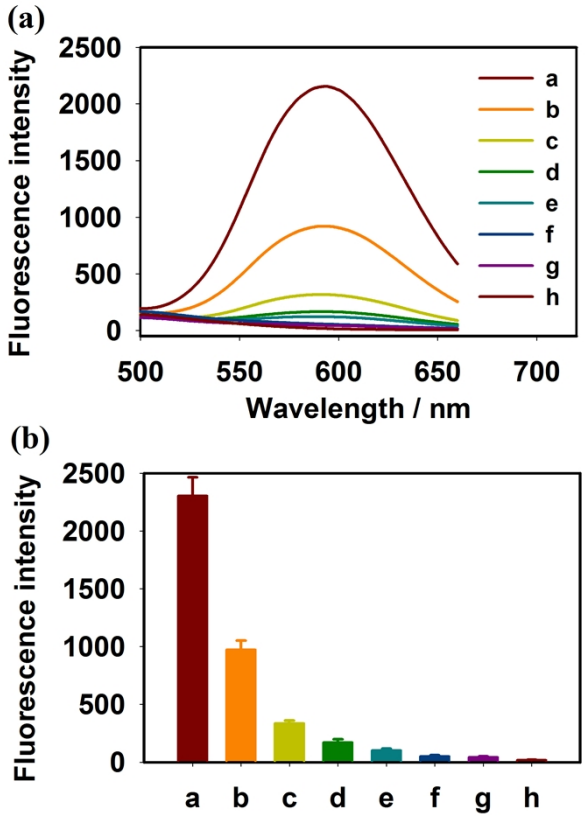

Fig. S7 (a) Fluorescence spectra and (b) intensity of fluorescent CuNPs templated by dsDNA with the same total length (22 bp), but different length of poly(AT-TA). a, ds(AT-TA)$_{22}$; b, ds(GC-CG)$_2$(AT-TA)$_{18}$(GC-CG)$_2$; c, ds(GC-CG)$_4$(AT-TA)$_{14}$(GC-CG)$_4$; d, ds(GC-CG)$_6$(AT-TA)$_{10}$ (GC-CG)$_6$; e, ds(GC-CG)$_8$(AT-TA)$_6$(GC-CG)$_8$; f, ds(GC-CG)$_{10}$(AT-TA)$_2$(GC-CG)$_{10}$; g, ds(GC- CG)$_{22}$; h, blank). The error bars represent the standard deviation of three independent measurements. Detailed sequence information of each dsDNA used here is listed in the Table S5.