Colorimetric recognition of DNA intercalator with unmodified gold nanoparticles

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Experimental Section

Materials. All oligodeoxyribonucleotides were purchased from Beijing SBS Genetech Co.,Ltd. (Beijing, China). $HAuCl_4·3H_2O$ was purchased from Aldrich Co.. Trisodium citrate, sodium chloride, sodium acetate and sodium phosphate monobasic dehydrate were purchased from tianjin fuchen chemistry reagent factory. $Ru(phen)_3Cl_2$ and Ethidium bromide was purchased from aldrich-sigma Co., $Ru(bipy)_2(dppz)(BF_4)_2·1.5H_2O$, $Ru(phen)_2(dppz)$ $(BF_4)_2·3.5H_2O$ and $Ru(bipy)_2(dppx)$ $(BF_4)_2·2H_2O$ was home made. The store solution of $1.0×10^{-4}$M $Ru(phen)_3^{2+}$ was prepared by dissolving 7.1mg $Ru(phen)_3Cl_2$ in 100ml water; $1.0×10^{-4}$ M Ethidium bromide was prepared by dissolving 4.0mg Ethidium bromide in 100ml water; $1.0×10^{-4}$M $Ru(bipy)_2(dppz)^{2+}$ was prepared by dissolving 9.0mg $Ru(bipy)_2(dppz)(BF_4)_2·1.5H_2O$ in 100ml water; $1.0×10^{-4}$M $Ru(phen)_2(dppz)^{2+}$ was prepared by dissolving 9.1mg $Ru(phen)_2(dppz)$ $(BF_4)_2·3.5H_2O$ in 100ml water; $1.0×10^{-4}$M $Ru(bipy)_2(dppx)^{2+}$ was prepared by dissolving 9.3mg $Ru(bipy)_2(dppx)$ $(BF_4)_2·2H_2O$ in 100ml water.

Ultraviolet-visible absorption spectra were recorded on TU 1901UV-visiable absorption spectrometer (Beijing Pukinje General Instrument Co.,Ltd) using 1 cm path length quartz cells. Nano-pure water (18.1 MΩ) that obtained from a 350 Nano-pure water system (Guangzhou Crystalline Resdurce Desalination of Sea Water and Treatment Co.,Ltd.) was used in all experiments.

Preparation of Au nanoparticles

Au nanoparticles were prepared with the method of reduction of $HAuCl_4$ with citrate [Grabar, K.C., Freeman, R.G., Hommer, M.B., Natan, M. J. Anal. Chem. 1995, 67, 735-743.]. The average particle size was about 13 nm in diameter by TEM.

Procedure

300 μL gold colloid was diluted with 300ul water, then was mixed with 150ul 1350pmol

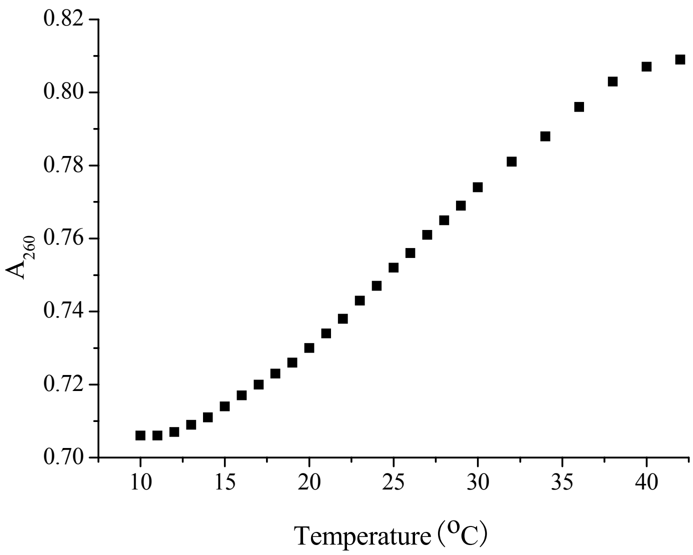
oligo-a (or oligo-b), then those intercalative (or non- intercalative) molecule were added into separately, and then with 300 μL of 10 mM PBS containing 0.35 M NaCl was added.

Measurement of melting temperature

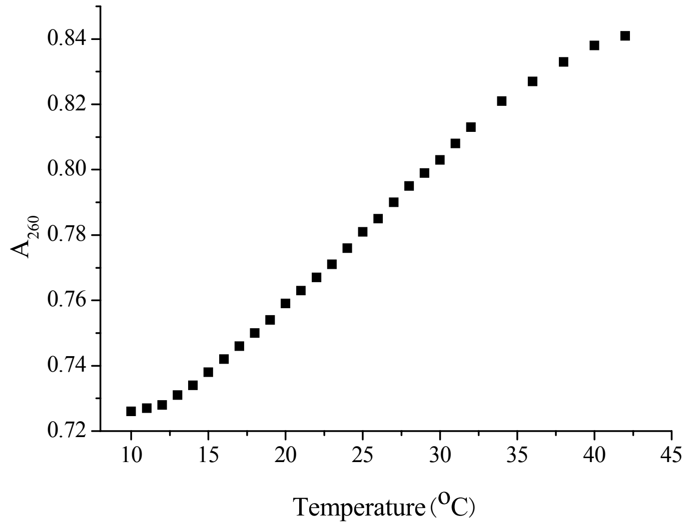
The melting curve of oligo-a with and without $Ru(phen)_3^{2+}$ was obtained with TU 1901UV-visiable absorption spectrometer (Beijing Pukinje General Instrument Co.,Ltd) using 1 cm path length quartz cells. The melting curve of oligo-a in the presence of EB, $Ru(bipy)_2dppz^{2+}$, $Ru(phen)_2dppz^{2+}$ or $Ru(bipy)_2dppx^{2+}$ was recorded with RF-5301(Shimadazu, Japan) spectrofluorometer with a quartz cell (1×1 cm cross-section).

S-Table 1 melting temperature of oligo-a in the presence of different ligand

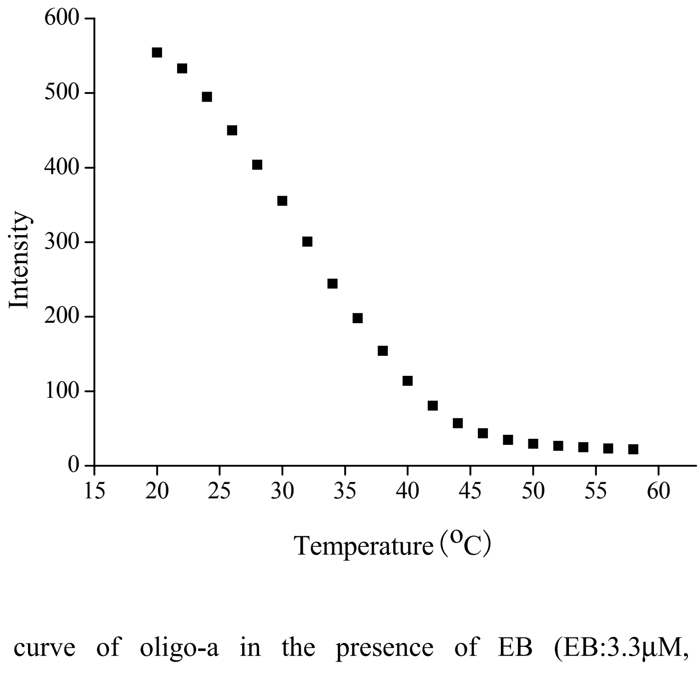
DNA binder	Tm (°C)
Oligo-a (no binder)	25
$Ru(phen)_3^{2+}$	26
EB	33
$Ru(bipy)_2dppz^{2+}$	44
$Ru(phen)_2dppz^{2+}$	44
$Ru(bipy)_2dppx^{2+}$	42



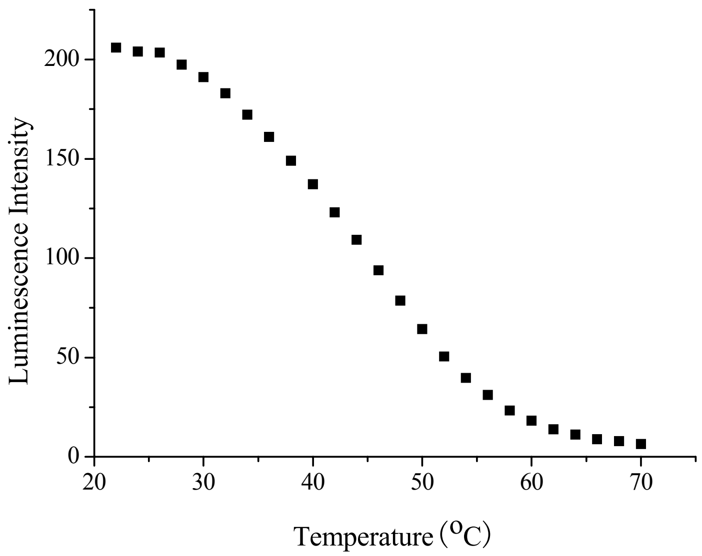
S-Figure-1 Melting curve of oligo-a(Oligo-a: 7.0μM, NaCl: 0.10M)



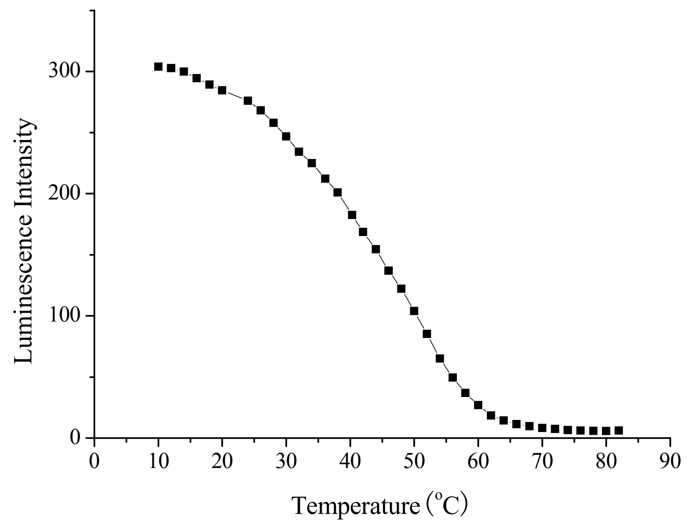
S-Figure-2 Melting curve of oligo-a in the presence of $Ru(phen)_3^{2+}$ (Oligo-a: 7.0μM, NaCl: 0.10M, $Ru(phen)_3^{2+}$:5.0μM)



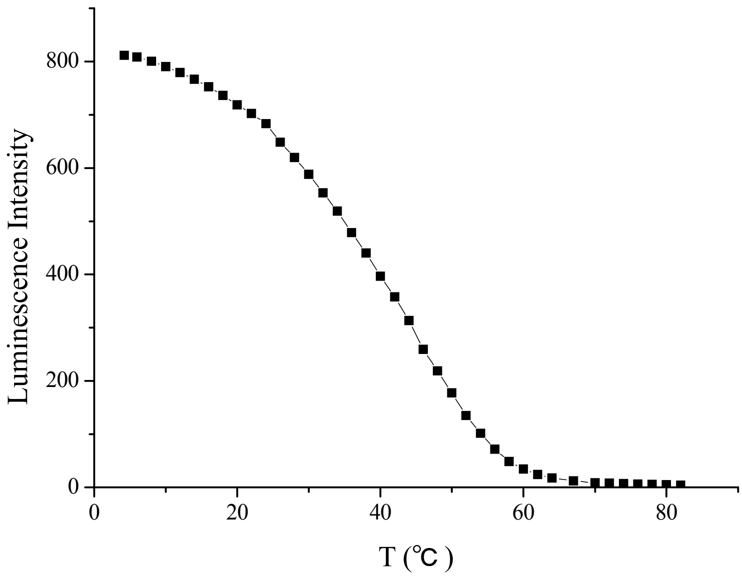
S-Figure-3 Melting curve of oligo-a in the presence of EB (EB:3.3μM, NaCl:0.1M , oligo-a:4.0μM,λ_{ex}:542nm λ_{em}:602nm),slit width(EX:3.0nm, EM:5.0nm)



S-Figure-4 Melting curve of oligo-a in the presence of $Ru(bipy)_2dppz^{2+}$ ($Ru(bipy)_2dppz^{2+}$:3.3μM ,NaCl:0.1M , oligo-a:1.3μM, λ_{ex}:455nm, λ_{em}:630nm), slit width(EX:5.0nm, EM:10.0nm)

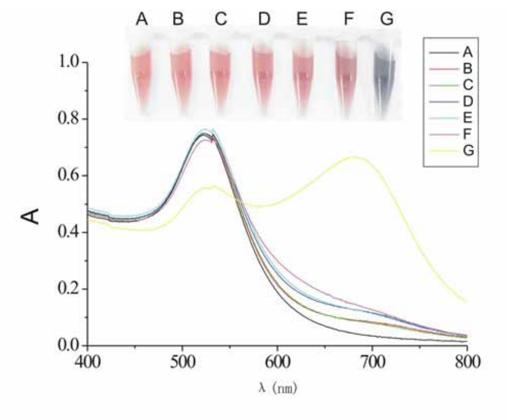


S-Figure-5 Melting curve of oligo-a in the presence of $Ru(phen)_2dppz^{2+}$ ($Ru(phen)_2dppz^{2+}$:3.3μM, NaCl:0.1M，oligo-a:4.0μM, λ_{ex}:449nm, λ_{em}:617nm), slit width (EX: 5.0nm, EM: 10.0nm)



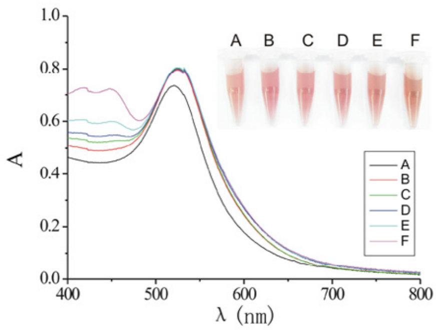
S-Figure-6 Melting curve of oligo-a in the presence of $Ru(bipy)_2dppx^{2+}$ ($Ru(bipy)_2dppx^{2+}$:3.3μM, NaCl:0.1M , oligo-a:4.0μM, λ_{ex}:460nm, λ_{em}:613nm), slit width(EX:5.0nm, EM:10.0nm)

1. $Ru(phen)_3^{2+}$:



S-Figure-7 Effect of $Ru(phen)_3^{2+}$on the naked gold nanoparticles.

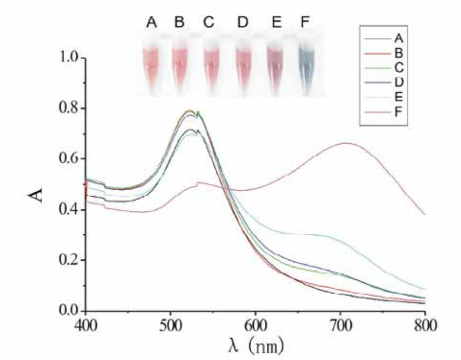
A. 3.0nM gold nanoparticles B. A+0.05μM $Ru(phen)_3^{2+}$
C. A+0.10μM $Ru(phen)_3^{2+}$; D. A+0.16μM $Ru(phen)_3^{2+}$
E. A+0.21μM $Ru(phen)_3^{2+}$ F. A+ 0.26μM $Ru(phen)_3^{2+}$
G.. A+0.31μM $Ru(phen)_3^{2+}$



S-Figure-8 Effect of $Ru(phen)_3^{2+}$ on the oligo-b adsorbed gold nanoparticles.

A. 3.0nM gold nanoparticles+1.13μM oligo-b; B. A+2.08μM $Ru(phen)_3^{2+}$;
C. A+4.00μM $Ru(phen)_3^{2+}$; D. A+5.21μM $Ru(phen)_3^{2+}$;
E. A+8.33μM $Ru(phen)_3^{2+}$; F. A+16.67μM $Ru(phen)_3^{2+}$

2. EB

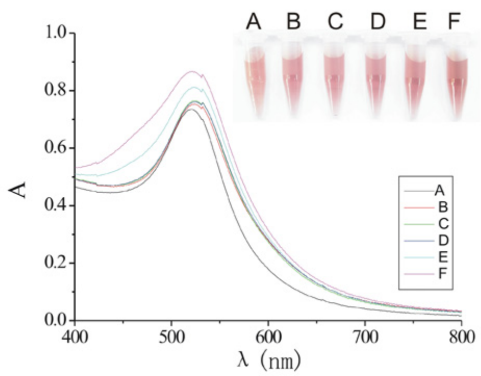


S-Figure-9 Effect of Ebon the naked gold nanoparticles

A.3.0 nM Au nanoparticles B. A+0.10 μM EB

C. A+0.21 μM EB D. A+0.42 μM EB

E. A+0.63 μM EB F. A+0.84 μM EB



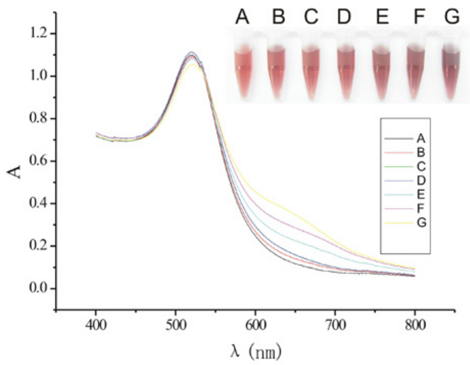
S-Figure-10 Effect of EB on the oligo-b adsorbed gold nanoparticles

A. 3.0 nM Au nanoparticles+1.13 μM oligo-b B. A+1.04 μM EB

C. A+2.08 μM EB D. A+4.00 μM EB

E. A+16.67 μM EB F. A+33.33 μM

3. $Ru(bipy)_2dppz^{2+}$



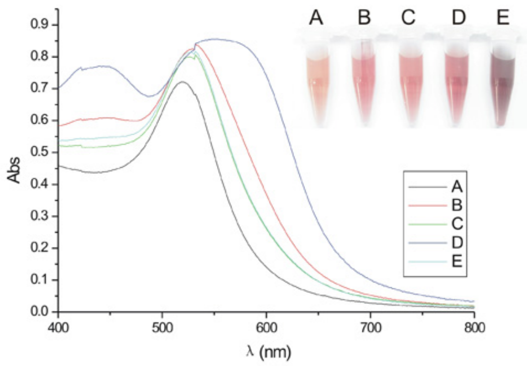
S-Figurre-11 Effect of $Ru(bipy)_2dppz^{2+}$on the naked gold nanoparticles

A. 3.0 nM Au nanoparticles B. A+0.03 μM $Ru(bipy)_2dppz^{2+}$

C. A+0.06 μM $Ru(bipy)_2dppz^{2+}$ D. A+0.09 μM $Ru(bipy)_2dppz^{2+}$

E. A+0.13 μM $Ru(bipy)_2dppz^{2+}$ F. A+0.16 μM $Ru(bipy)_2dppz^{2+}$

G. A+0.21 μM $Ru(bipy)_2dppz^{2+}$



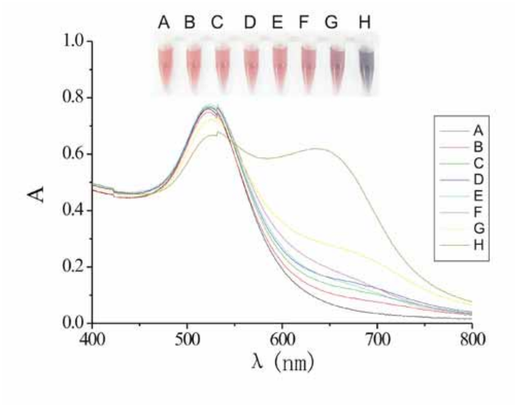
S-Figure-12 Effect of $Ru(bipy)_2dppz^{2+}$on the oligo-b adsorbed gold nanoparticles

A. 3.0 nM Au nanoparticles+1.13 μM oligo-b B. A+4.0 μM $Ru(bipy)_2dppz^{2+}$

C. A+5.21 μM $Ru(bipy)_2dppz^{2+}$ D. A+8.33 μM $Ru(bipy)_2dppz^{2+}$

E. A+16.67 μM $Ru(bipy)_2dppz^{2+}$

4. $Ru(phen)_2dppz^{2+}$:



S-Figure-13 Effect of $Ru(phen)_2dppz^{2+}$on the naked gold nanoparticles

A. 3.0 nM Au nanoparticles

B. A+0.03 μM $Ru(phen)_2dppz^{2+}$

C. A+0.06 μM $Ru(phen)_2dppz^{2+}$

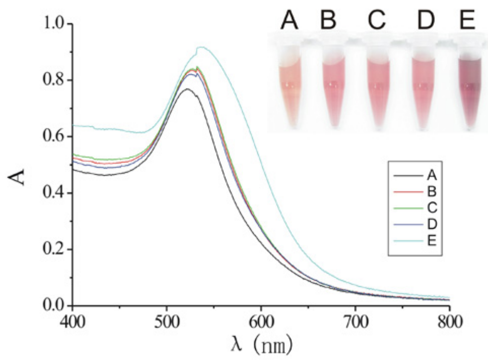
D. A+0.09 μM $Ru(phen)_2dppz^{2+}$

E. A+0.13 μM $Ru(phen)_2dppz^{2+}$

F. A+0.21 μM $Ru(phen)_2dppz^{2+}$

G. A+0.27 μM $Ru(phen)_2dppz^{2+}$

H. A+0.31 μM $Ru(phen)_2dppz^{2+}$



.S-Figure-14 Effect of $Ru(phen)_2dppz^{2+}$on the oligo-b adsorbed gold nanoparticles

A. 3.0 nMAu nanoparticles+1.13 μM oligo-b

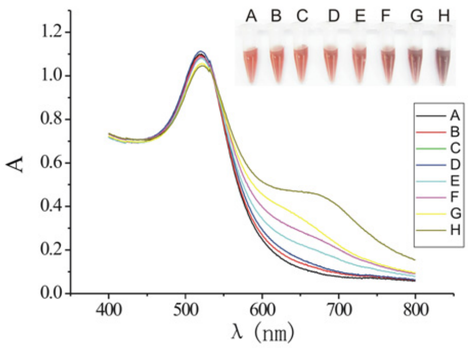
B. A+2.20 μM $Ru(phen)_2dppz^{2+}$

C. A+3.13 μM $Ru(phen)_2dppz^{2+}$

D. A+4.17 μM $Ru(phen)_2dppz^{2+}$

E. A+8.33 μM $Ru(phen)_2dppz^{2+}$

5. $Ru(bipy)_2dppx^{2+}$:



S-Figure -15 Effect of $Ru(bipy)_2dppx^{2+}$on the naked gold nanoparticles

A. 3.0 nM Au nanoparticles

B. A+0.011 μM $Ru(bipy)_2dppx^{2+}$

C. A+0.023 μM $Ru(bipy)_2dppx^{2+}$

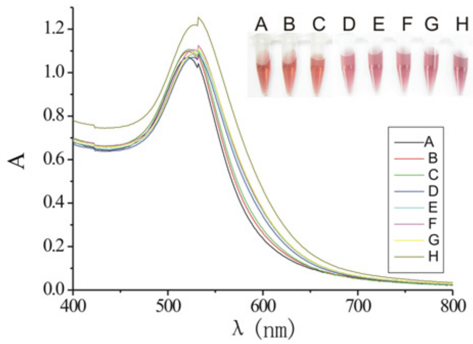
D. A+0.034 μM $Ru(bipy)_2dppx^{2+}$

E. A+0.057 μM $Ru(bipy)_2dppx^{2+}$

F. A+0.12 μM $Ru(bipy)_2dppx^{2+}$

G. A+0.17 μM $Ru(bipy)_2dppx^{2+}$

H. A+0.23 μM $Ru(bipy)_2dppx^{2+}$



S-Figure-16 Effect of $Ru(bipy)_2dppx^{2+}$ on the oligo-b adsorbed gold nanoparticles

A. 3.0 nM Au nanoparticles+1.13 μM oligo-b

B. A+0.17 μM $Ru(bipy)_2dppx^{2+}$

C. A+0.33 μM $Ru(bipy)_2dppx^{2+}$

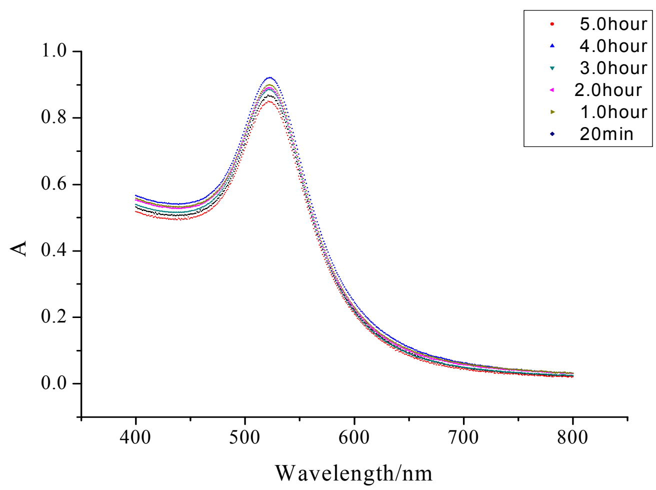
D. A+2.08 μM $Ru(bipy)_2dppx^{2+}$

E. A+2.40 μM $Ru(bipy)_2dppx^{2+}$

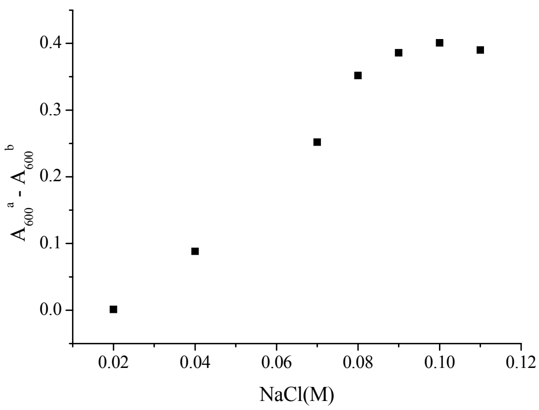
F. A+2.50 μM $Ru(bipy)_2dppx^{2+}$

G. A+2.71 μM $Ru(bipy)_2dppx^{2+}$

H. A+3.13 μM $Ru(bipy)_2dppx^{2+}$



S-Figure-17 Effect of incubation time on the absorption spectra of AuNPs-oligo a
1.3μM oligo a, 3.0nM AuNPs, 0.1 M NaCl

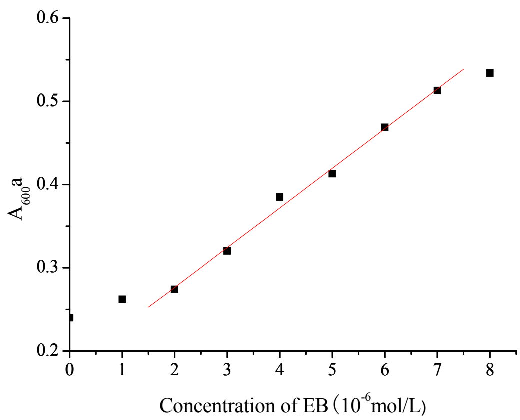


S-Figure-18 Effect of NaCl on the aggregation of AuNPs-oligo a and AuNPS-oligo b.

1.30 μM oligo-a, 1.30 μM oligo-b, 3.0 nM AuNPs, 4.0μM $Ru(bipy)_2dppz^{2+}$:

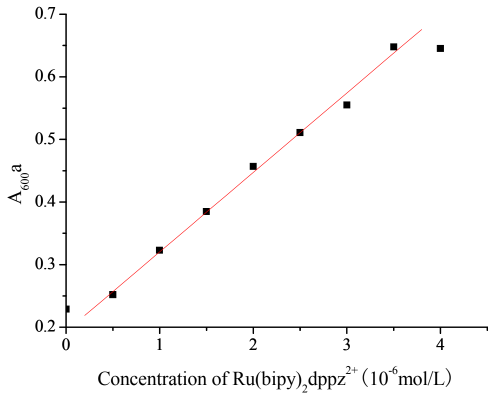
S-Table 2 Analytical parameters for detection intercalators

Intercalators	Linear regression equation(C,μmol/L)	Linear range (μmol/L)	r(Correlation coefficient)	Precision at 0.5μmol/L (RSD, %)
EB	A=0.181+0.0477C	2.0-7.0	0.9969	2.86
$Ru(bipy)_2dppz^{2+}$	A=0.193+0.127C	0.5-3.5	0.9973	3.55
$Ru(phen)_2dppz^{2+}$	A=0.078+0.169C	1.0-4.0	0.9955	3.34
$Ru(bipy)_2dppx^{2+}$	A=0.126+0.177C	1.0-3.5	0.9958	2.84



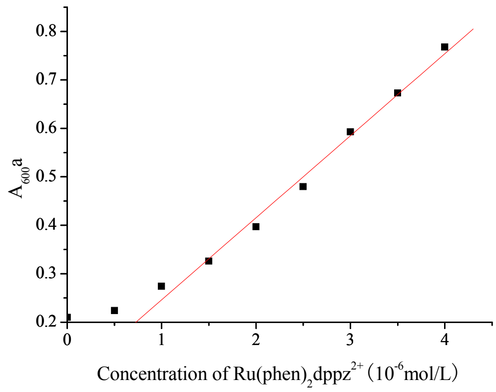
S-Figure 19 Effect of EB concentration on the absorbance of AuNPs-oligo a.

oligo-a: 1.30 μM; gold nanoparticles:3.0 nM



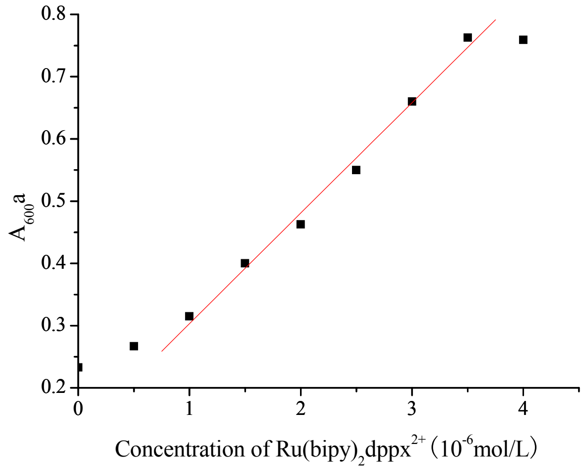
S-Figure 20 Effect of $Ru(bipy)_2ddpz^{2+}$ concentration on the absorbance of AuNPs-oligo a.

oligo-a: 1.30 µM; gold nanoparticles:3.0 nM



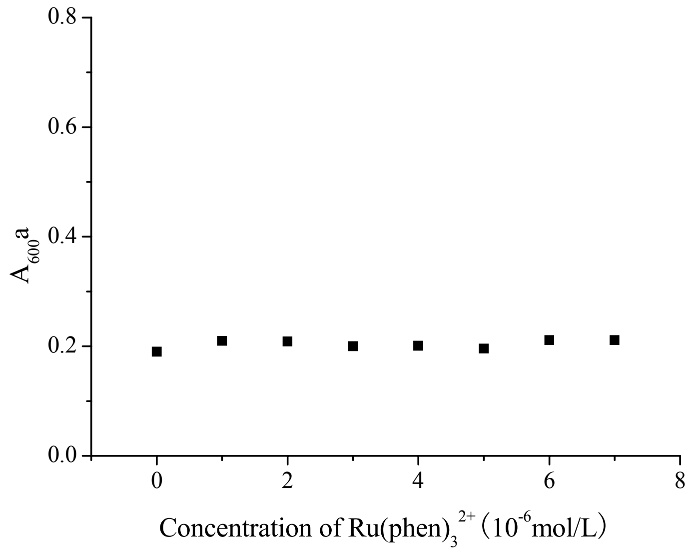
S-Figure 21 Effect of $Ru(phen)_2ddpz^{2+}$ concentration on the absorbance of AuNPs-oligo a.

oligo-a: 1.30 µM; gold nanoparticles:3.0 nM



S-Figure 22 Effect of $Ru(bipy)_2ddpx^{2+}$ concentration on the absorbance of AuNPs-oligo a.

oligo-a: 1.30 µM; gold nanoparticles:3.0 nM



S-Figure 23 Effect of $Ru(phen)_3^{2+}$ concentration on the absorbance of AuNPs-oligo a.

oligo-a: 1.30 μM; gold nanoparticles:3.0 nM