Electronic Supplementary Information

Label-free fluorescent DNA sensor for the detection of silver ions based on molecular light switch Ru complex and unmodified quantum dots

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Experimental

Reagents and materials

The C-ssDNA (5' CTC TCT CCA ACC TCT CTC 3') was synthesized from Shanghai Sangon Biotechnology Co. Ltd. (Shanghai, China) and used without further purification. DNA stock solution was obtained by dissolving oligonucleotides in 10 mM HEPES-NaOH buffer (pH 7.4) and was stored at 4 ℃ before use. The concentration of oligonucleotide was determined using the absorbance at 260 nm. $Ru(bpy)_2dppz^{2+}$ was prepared and characterized according to the literature.[1] Thioglycolic acid (≥ 98%), $CdCl_2$ (99.99%), tellurium powder (99.99%), $NaBH_4$ (95%) were obtained from Sigma-Aldrich. All other reagents were of analytical grade. All measurements were performed in 10 mM HEPES-NaOH buffer (pH 7.4). The water used was purified by Milli-Q (18 MΩ/cm).

Apparatus

Lambda Bio 40 UV/Vis Spectrophotometer (Perkin-Elmer, USA) was used to quantify the oligonucleotides and QDs. The PL spectra were recorded at room temperature on an F-7000 fluorescence spectrophotometer (Hitachi) with a quartz cell (2 mm). The excitation and emission slit width were both 10 nm.

Synthesis of TGA-capped CdTe quantum dos

The synthesis of CdTe QDs was performed according to the reference with some modification.[2] First, NaHTe was prepared by adding 40 mg $NaBH_4$ to a flask containing 46 mg tellurium powder and 2 mL Milli-Q water under nitrogen atmosphere. The reaction was kept on for several hours until all tellurium powder was dissolved. 0.092 g (0.5 mmol) of $CdCl_2$ and 0.092 g (1 mmol) of thioglycolic acid were dissolved in 100 mL Milli-Q water, followed by adjusting pH to 8.2 by addition of 1 M NaOH solution. The mixture was deaerated by N_2 bubbling for 30 min. Then NaHTe solution (0.062 mmol) was quickly injected into the mixture under vigorous stirring, followed by refluxing the mixture for 2 h under open-air conditions.

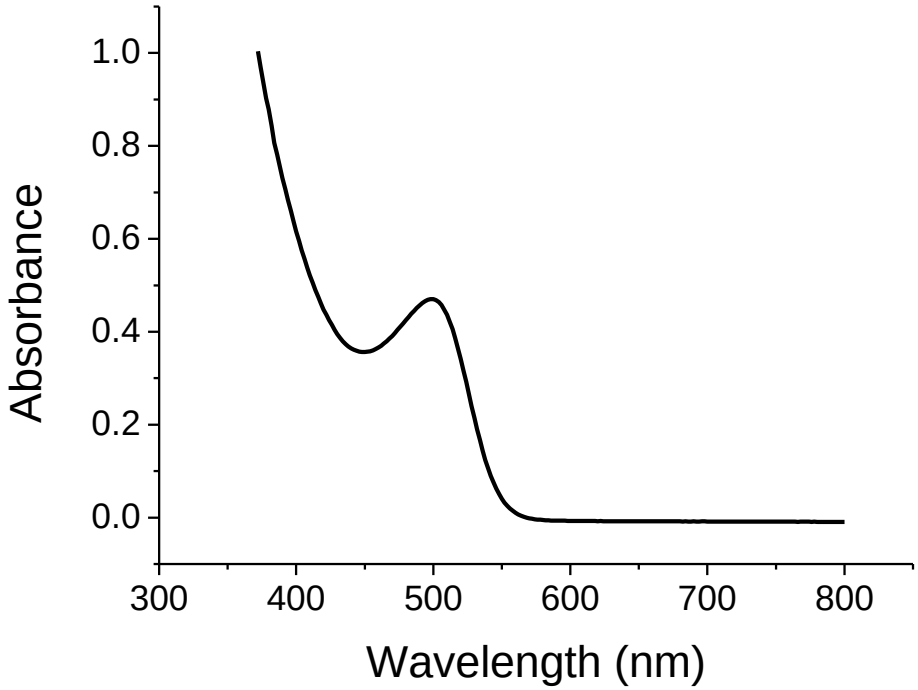

Fig. S1 UV-vis absorption spectrum of CdTe QDs aqueous solution.

The UV-vis spectrum of TGA-capped CdTe QDs was obtained (Fig. S1). According to the following empirical equations, the sizes and concentrations of QDs can be estimated from the adsorption peaks in UV-vis spectrum.[3] The size of TGA-capped CdTe QDs is 2.34 nm diameter. The concentration of QDs is 7697.43 nM.

D (nm) = $(9.8127\times10^{-7})\ \lambda^3 - (1.7147\times10^{-3})\ \lambda^2 + (1.0064)\lambda - (194.84)$

C (mol L^{-1}) = A/ [10043 $(D)^{2.12}l$]

Fluorescence experiments

For the detection of the quenching behavior of $Ru(bpy)_2(dppz)^{2+}$ on the fluorescence of QDs, 750 nM TGA-capped CdTe QDs and various amounts of $Ru(bpy)_2(dppz)^{2+}$ were incubated in 10 mM HEPES-NaOH buffer (pH 7.4) at room temperature for 5 min in a 0.5 mL Eppendorf tube respectively, then the fluorescence spectra were measures in a 500 μL quartz cuvette at room temperature.

For the fluorescence assay of metal ions, 10 μM C-ssDNA was incubated with different concentration of metal ions for 30 min, and then 10 μM $Ru(bpy)_2(dppz)^{2+}$ was added to allow it bind to DNA for 5 min. Next, 750 nM CdTe QDs was mixed with this solution and incubated at room temperature for 5 min. The resulting solutions were studied by fluorescent spectroscopy.

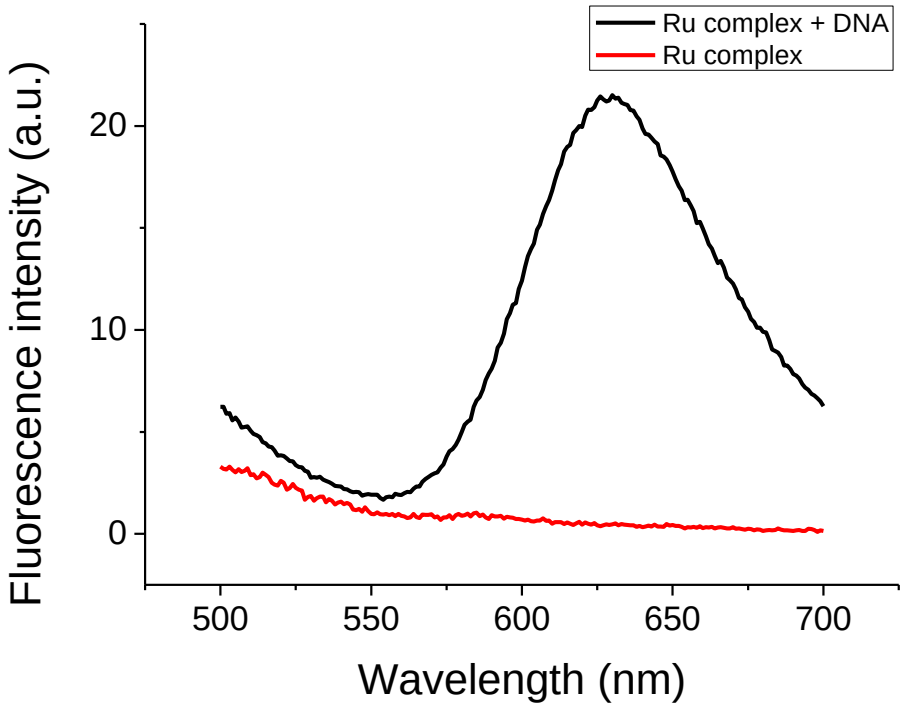

Fig. S2 Fluorescence emission spectra of 10 μM $Ru(bpy)_2(dppz)^{2+}$ in the absence and presence of 10 μM DNA. Excitation: 365 nm.

References

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2. H. Peng, L. Zhang, T. H. M. Kjällman and C. Soeller, *J. Am. Chem. Soc.*, 2007, **129**, 3048-3049.
3. W. W. Yu, L. Qu, W. Guo and X. Peng, *Chem. Mater.*, 2003, **15**, 2854-2860.