Electronic Supplementary Material (ESI) for RSC Advances

Direct Conjugation of DNA to Quantum Dots for Scalable Assembly of Photoactive Thin Films

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SUPPORTING INFORMATION

DNA sequences

DNA (polythymine) attached on QDs
5'DNA: 5'- /5'ThioMC6-D/TTT TTT TTT T -3'
3'DNA: 3'-/ 3'ThioMC3-D/TTT TTT TTT T -5'

Linker DNA (polyadenine)
5'A_{10}: 5'-AAA AAA AAA A -3'

*A length of DNAs was designed to be short enough in order to get QDs closer for efficient charge transport, prevent oxidation and allow salt stability. It is also importance to have enough number of bases to get hybridized with linker DNAs as well as allow freedom in motion of QDs during humid annealing.[1] Thymine was the most flexible base and identical bases(T_{10}/A_{10}) allows more flexibility in sharing linker DNAs between 5'T_{10} and 3'T_{10}-QDs by "sliding".

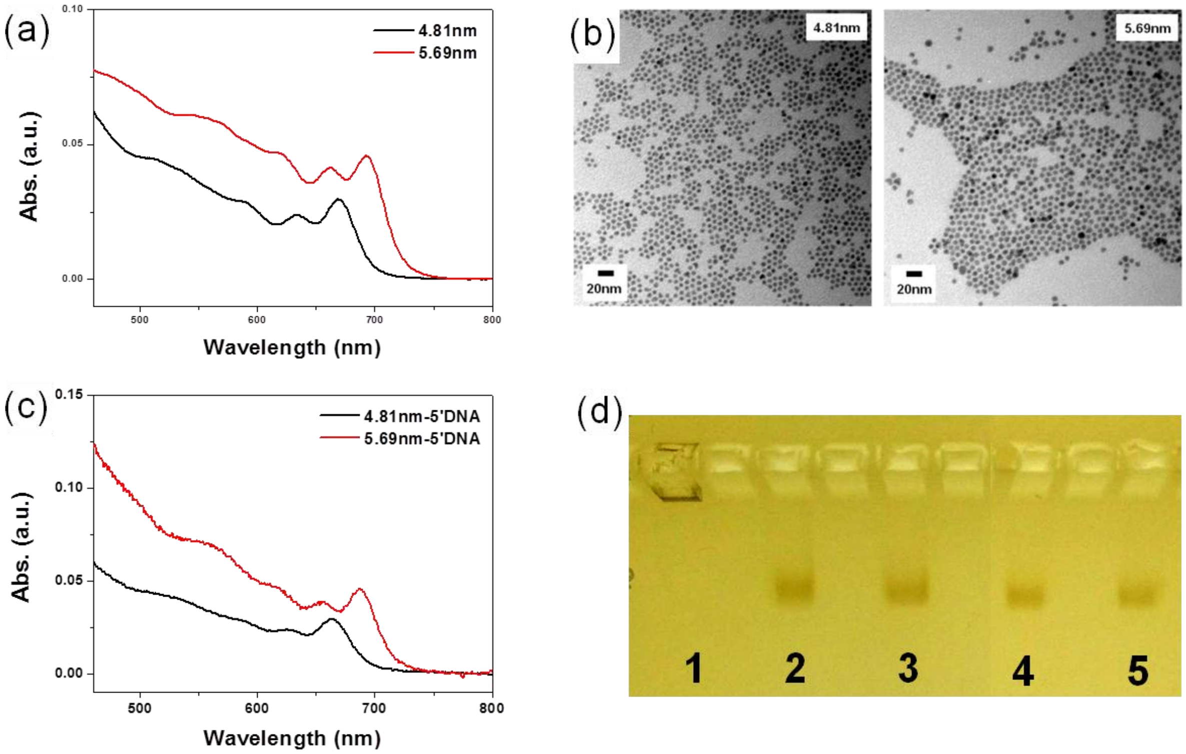
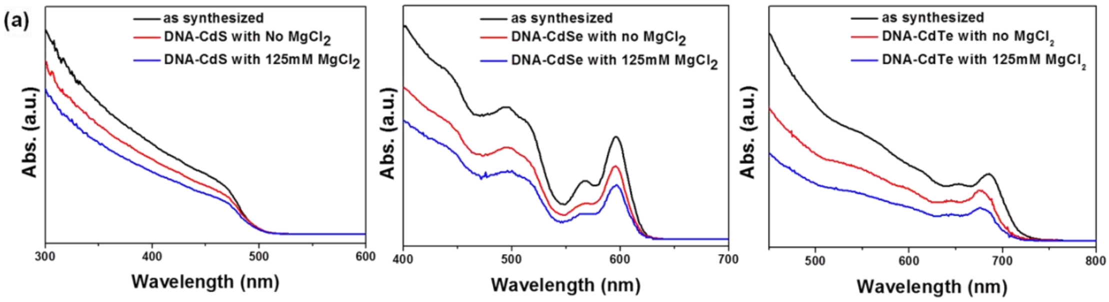


Figure S1. (a) UV-Vis absorbance of the as-synthesized 4.81nm, 5.69nm CdTe QDs. (b) TEM images of as-synthesized CdTe QDs. (c) UV-Vis absorbance of DNA(T_{10})-QD solutions. (d) Agaroase gel electrophoresis of Thioglycerol-QD and DNA(T_{10})-QDs, 1: Thioglycerol-QD, 2: 5’T_{10}-4.81nm CdTe, 3: 5’T_{10}-5.69nm CdTe, 4: 3’T_{10}-4.81nm CdTe, 5: 3’T_{10}-5.69nm CdTe.



CdS	Onset wavelength (nm)	CdSe	First peak of absorption/Onset wavelength (nm)	CdTe	First peak of absorption/Onset wavelength (nm)
as synthesized	527	as synthesized	596/629	as synthesized	720/684
DNA-CdSe with no $MgCl_2$	527	DNA-CdSe with no $MgCl_2$	596/629	DNA-CdSe with no $MgCl_2$	711/676
DNA-CdSe with 125mM $MgCl_2$	527	DNA-CdSe with 125mM $MgCl_2$	596/629	DNA-CdSe with 125mM $MgCl_2$	711/676

(b)

Peak diameter (nm)			
$MgCl_2$ (mM)	CdSe	CdTe	CdS
0	11.67	12.51	10.67
5	10.77	10.96	11.00
25	12.53	11.15	11.26
50	14.98	12.81	10.51
125	16.12	12.36	10.72

Figure S2. (a) UV-Vis absorbance of the as-synthesized QDs, DNA-QDs and DNA-QDs with 125mM $MgCl_2$ for CdS, CdSe and CdTe (top) and its summary of onset and first peak of absorption for QD, DNA-QD solutions. (bottom) (b) Summary of DLS measurement for DNA-QD solution as a function of $MgCl_2$ concentration

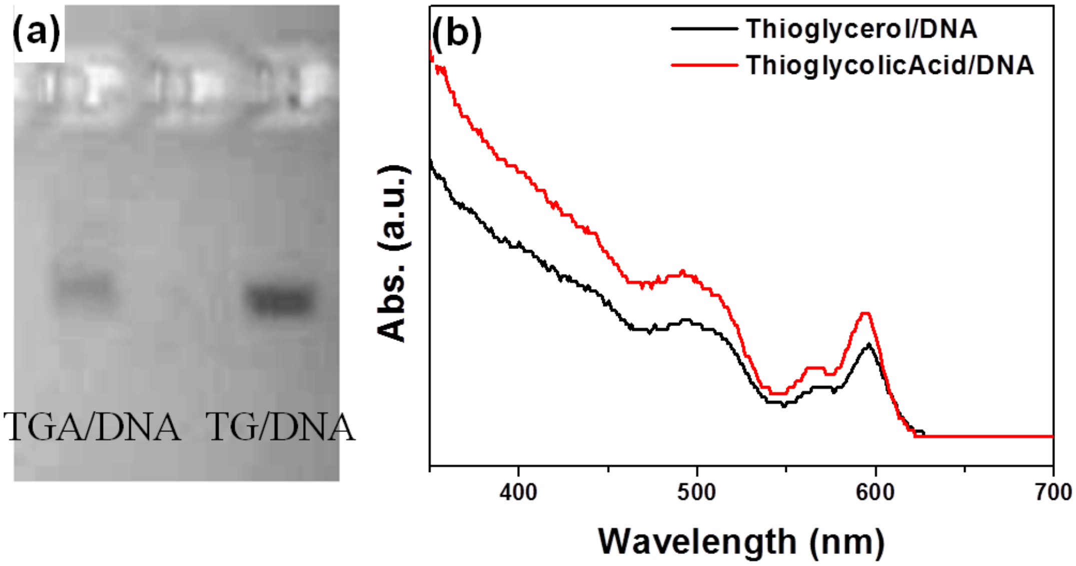


Figure S3. (a) Agaroase gel electrophoresis(1.5%) of DNA-Thioglycolic acid (TGA)-CdSe(left) and DNA-Thioglycerol (TG)-CdSe(right) showing less yields of DNA-Thioglycolic acid-CdSe solution. (b) UV-Vis absorbance of DNA-Thioglycolic acid-CdSe and DNA-Thioglycerol-CdSe showing a blue shift (oxidation) from DNA-Thioglycolic acid-CdSe solution.

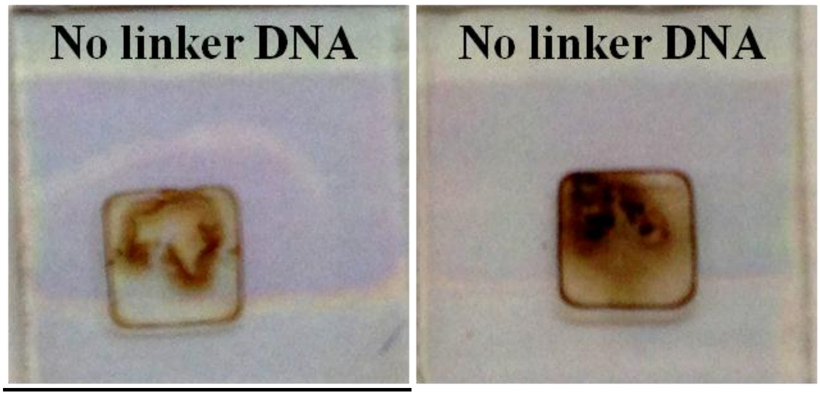


Figure S4. DNA-CdTe QD films produced when no linker DNA was added at 1.5 μM and 3 μM DNA-CdTe concentrations.

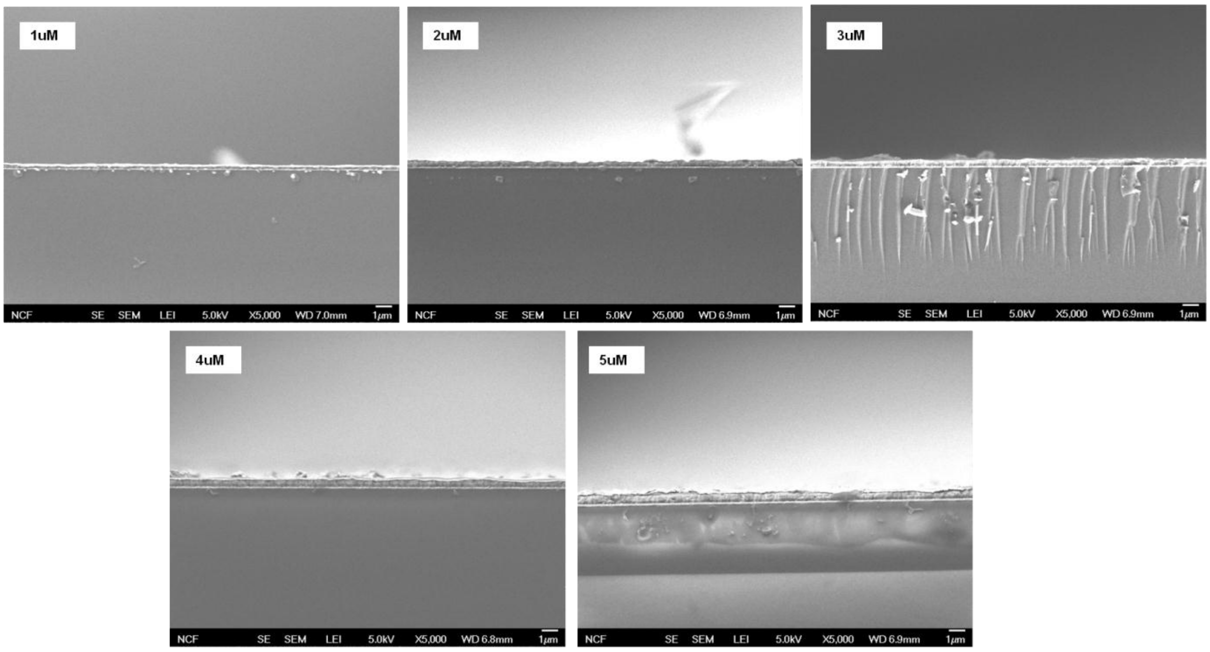


Figure S5. SEM images of low magnification of DNA(T_{10})-QD films from all different concentrations.

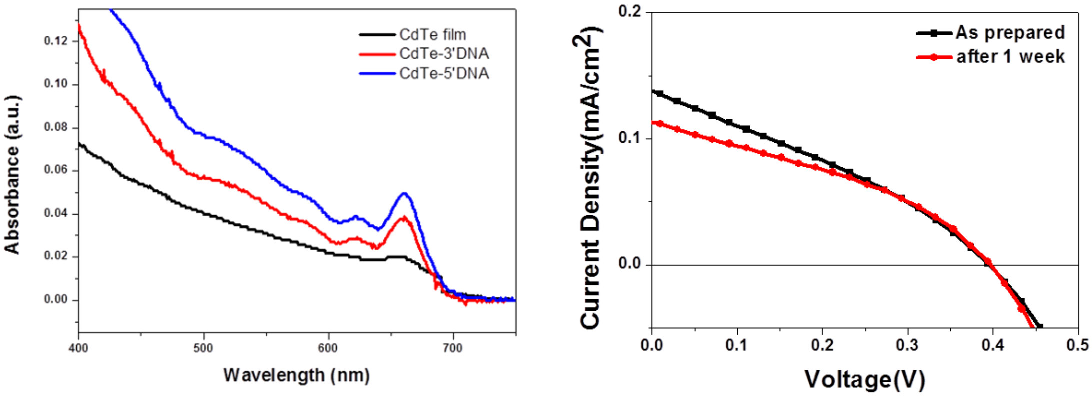


Figure S6. DNA-CdTe QDs films were robust against oxidation. (Left) The UV-Vis data of the prepared films showed no change in the absorption onset peak after QD film preparation. (Right) Current-Voltage measurement after a week showed minimal decrease in J_{sc} and V_{oc} was held constant.

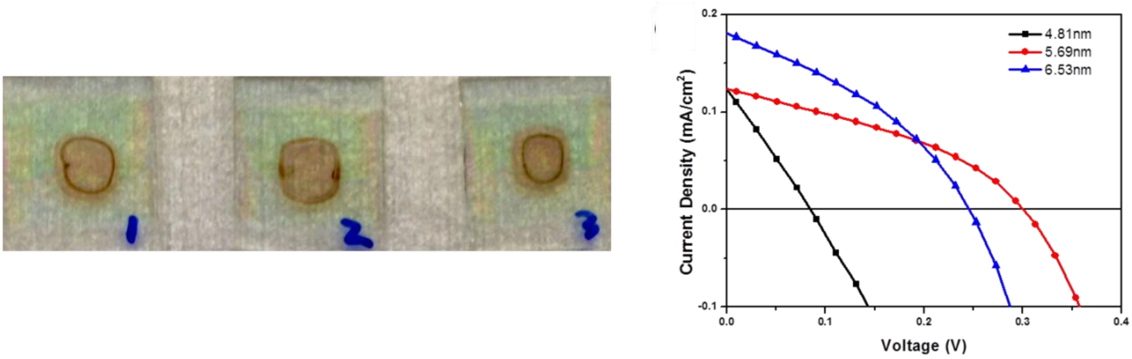


Figure S7. Films created by drying 3 different sizes of DNA CdTe QD onto TiO_2 with no linker DNA. **(#1**: 4.81 nm, #2: 5.69 nm and #3: 6.53 nm). IV curves obtained from DNA-CdTe films with no linker DNA shown on right.

Calculation of number of DNAs attached to QDs after conjugation

It was determined by UV-Vis absorbance. We have number of input ssDNA and QD, collect supernatant of unbound free ssDNA after DNA-QD conjugation, calculate total number of ssDNA bound to QD and number of ssDNAs per QD was obtained by dividing ssDNA bound to QDs by total number of QDs in solution.

ex. For 6.53nm CdTe, input ssDNA: 65.93 nmoles, input QDs: 0.184 nmole
collected unbound free ssDNA from supernatant: 62.16 nmoles

Thus, number of DNA on QD = (input ssDNA - unbound ssDNA) / number of QDs
= (65.93-62.16) / 0.184
= about 20.48

Approximately, 20 ssDNAs are attached on quantum dot.

Correlation between short circuit current (J_{sc}) and QD size

From ***ASTM G173-03 Reference Spectra Derived from SMARTS v. 2.9.2***

Absorbed input power for different sized CdTe QDs (larger than its bandgap)
under 1 Sun condition (100mW/cm^2)

Absorbed P_{input} (4.81nm) = 48.1mW/cm^2
Absorbed P_{input} (5.69nm) = 51.3mW/cm^2
Absorbed P_{input} (6.53nm) = 53.5mW/cm^2
Absorbed power increase (baseline: Absorbed P_{input} (4.81nm)):
3.2mW/cm^2 for 5.69nm QD, 5.4mW/cm^2 for 6.53nm QD

Assuming FF and V_{oc} values are similar enough to see a correlation only between J_{sc} and input power, J_{sc} increase of 0.058mA/cm^2(5.69nm QD) and 0.138mA/cm ^{2}(6.53nm QD) is corresponding to P_{input} increase of 3.2mW/cm^2 (5.69nm QD) and 5.4mW/cm^2(6.53nm). J_{sc} (0.242mA/cm^2) of 6.53nm QD is higher than a value(0.202mA/cm^2) calculated by a simple linear proportionality of an increase of P_{input}, which is attributed to an incorporation with a smaller conduction band offset to decrease a loss of the electron energy by the conduction band step that forms.[2]

QD size	V_{oc}(mV)	J_{sc}(mA/cm^2)	FF(%)
4.81nm	406	0.104	32.21
5.69nm	386	0.162	32.77
6.53nm	378	0.242	34.13

Reference

1. Macfarlane, R.; Lee, B.; Jones, M. R.; Harris, N.; Schatz, G. C.; Mirkin, C. A. *Science* **2011**, *334*, 204-208.

2. Tiefenbachera, T.; Pettenkofer, C.; Jaegermann, W. *J. Appl. Phys.* **2002**, *91*, 1984-1987.