Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

[Supplementary information]

Evidence of Homo-FRET in Quantum Dot-Dye Hetrostructured Assembly

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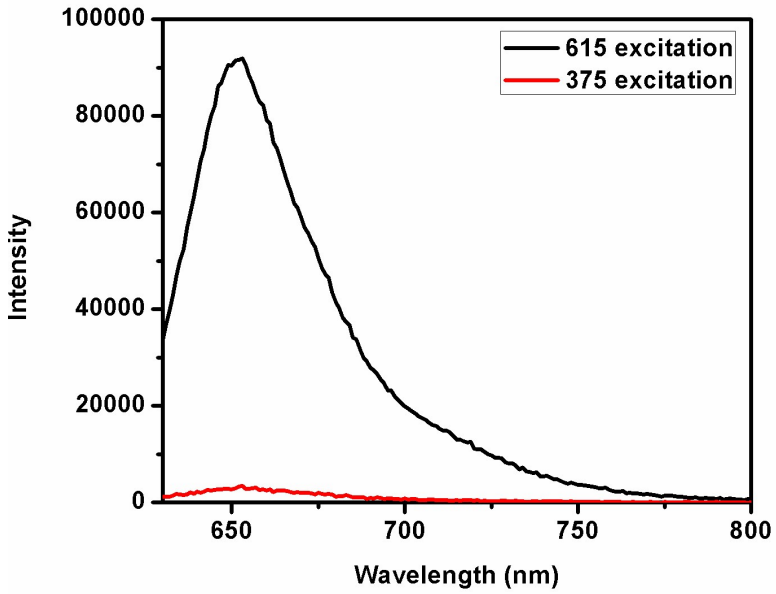


Fig. S1 The emission spectra of Ox170 at the excitation wavelengths of 375nm and 615nm. The concentration of Ox170 ~ 0.5×10^{-6} M.

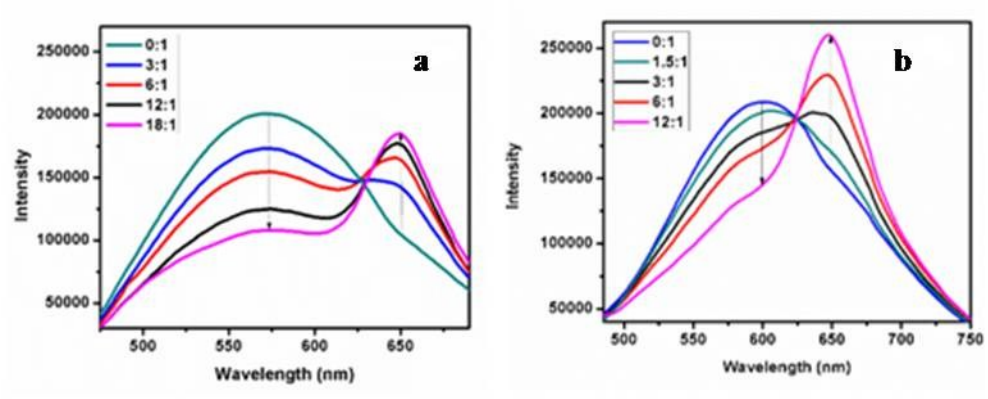


Fig. S2 Steady-state photoluminescence quenching of QDs (donor) in the presence of acceptor Ox170 : (a) 4.0 nm CdS, and (b) 4.4 nm CdS QDs at different Ox170:CdS ratios (legend shows dye:QD ratios in terms of molar concentration).

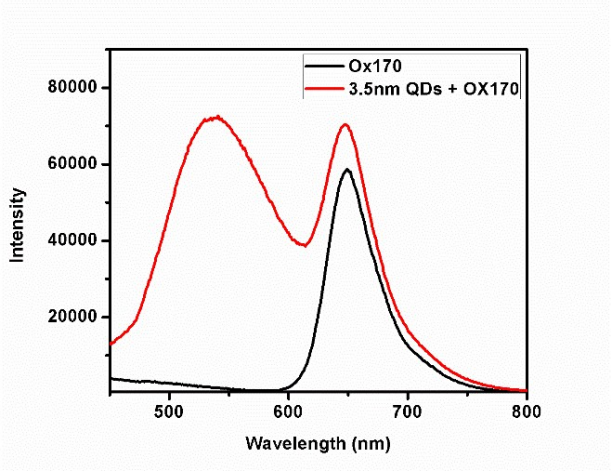


Fig. S3 Comparison between emission intensity of Ox170 and Ox170 in presence of 3.5nm QDs at the same concentration of Ox170 (~ 5×10^{-6} M). $\lambda exc.$ = 375 nm.

Table S1. The stoichiometry and absolute concentration of Ox170

Dye: QD (4.4 nm)	Concentration of Ox170 in Cuvette. (μM)	Dye: QD (4.0 nm)	Concentration of Ox170 in Cuvette. (μM)	Dye: QD (3.0 nm)	Concentration of Ox170 in Cuvette. (μM)
12:1	3.33	18:1	3.82	21:1	3.42
6:1	1.67	12:1	2.54	18:1	2.93
3:1	0.83	6:1	1.72	12:1	1.96
1.5:1	0.42	3:1	0.64	6:1	0.98

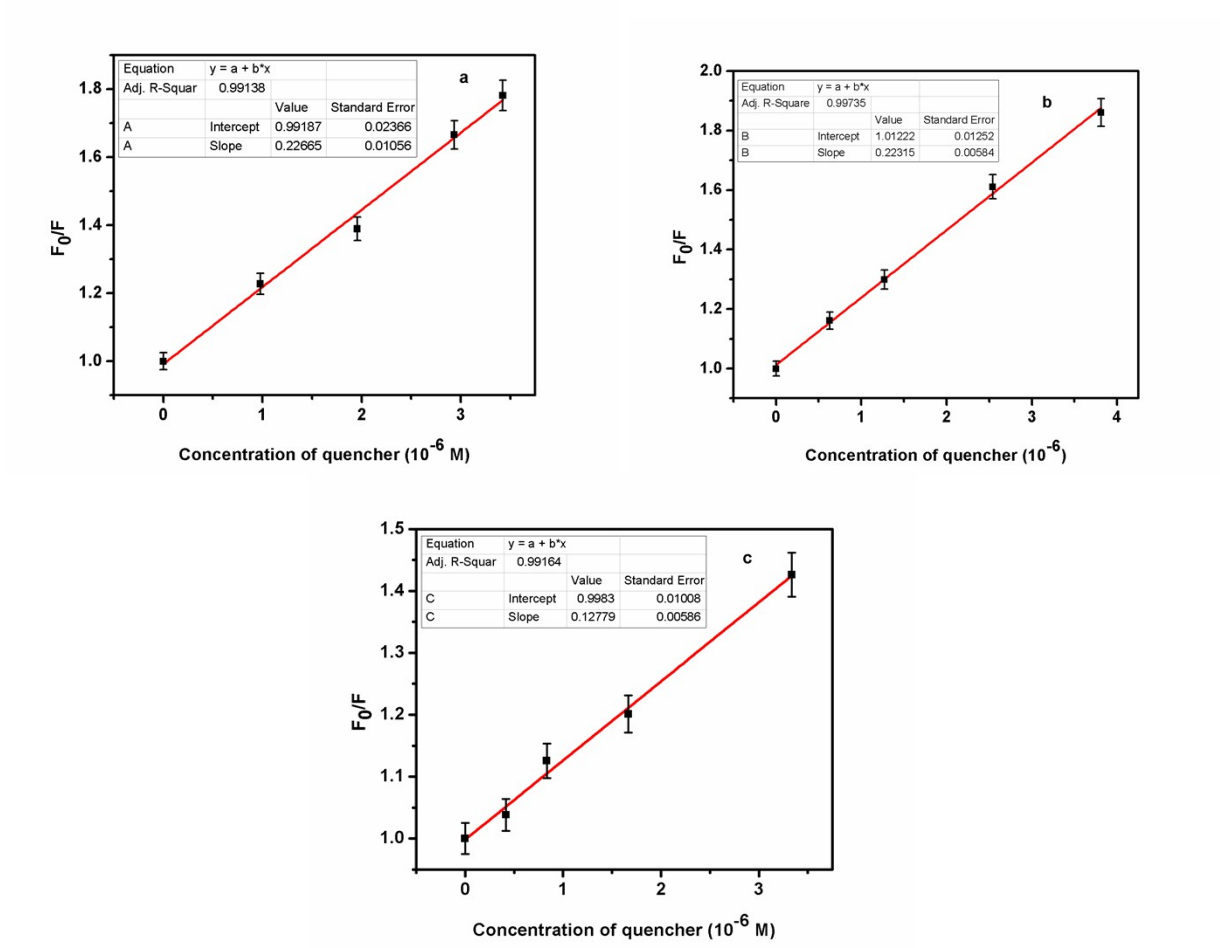


Fig. S4 Stern-Volmer plots associated with (a) 3.5 nm, (b) 4.0 nm, and (c) 4.4 nm QDs. The ±3% error bar added to the data points to indicate the accuracy of the fitting.

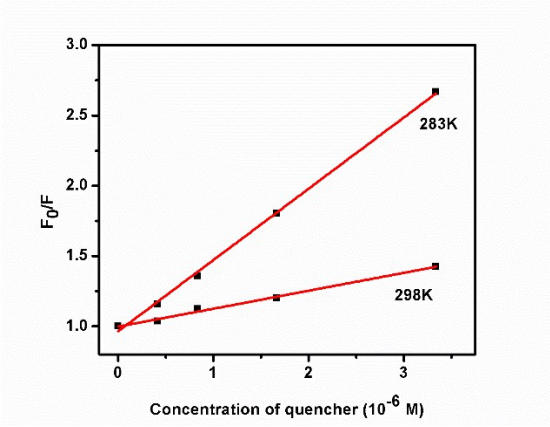


Fig. S5 Stern-volmer plots associated of 4.4 nm QDs in presence of Ox170 at 283K and 298K (RT). Decrease in slope of stern-volmer plot indicates quenching is predominantly static in nature.

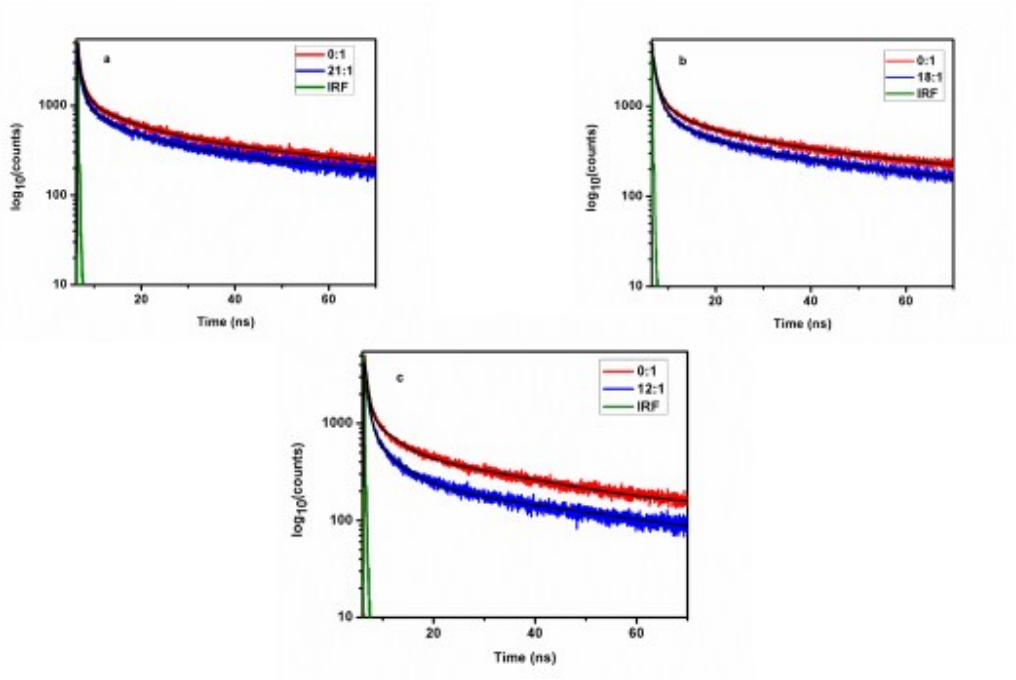
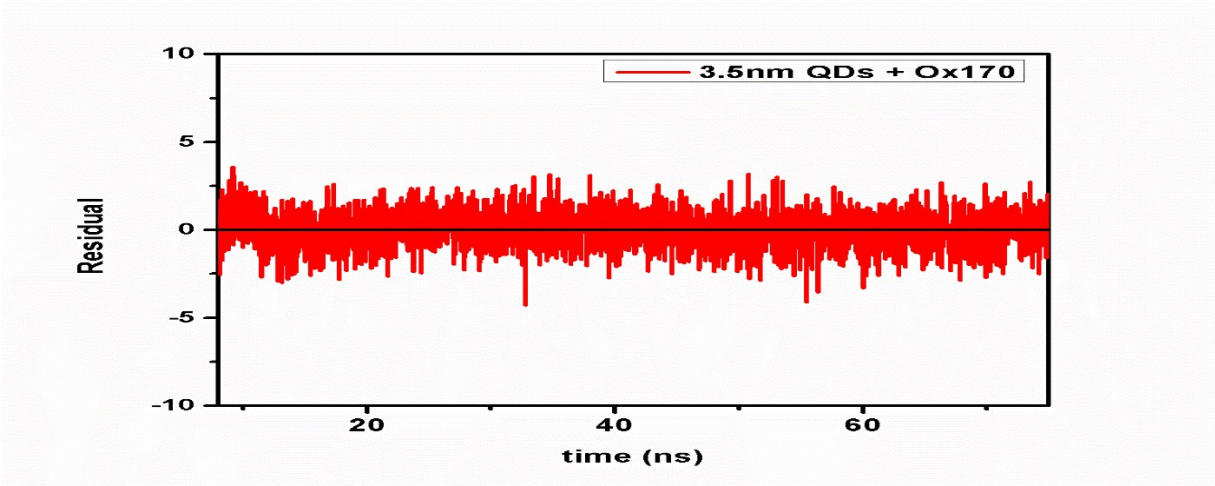
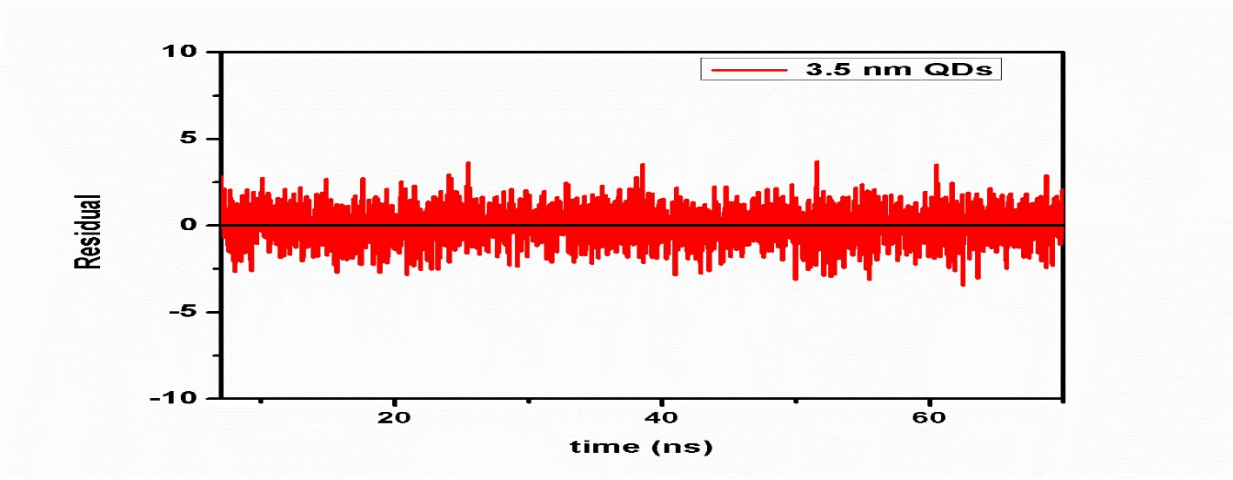
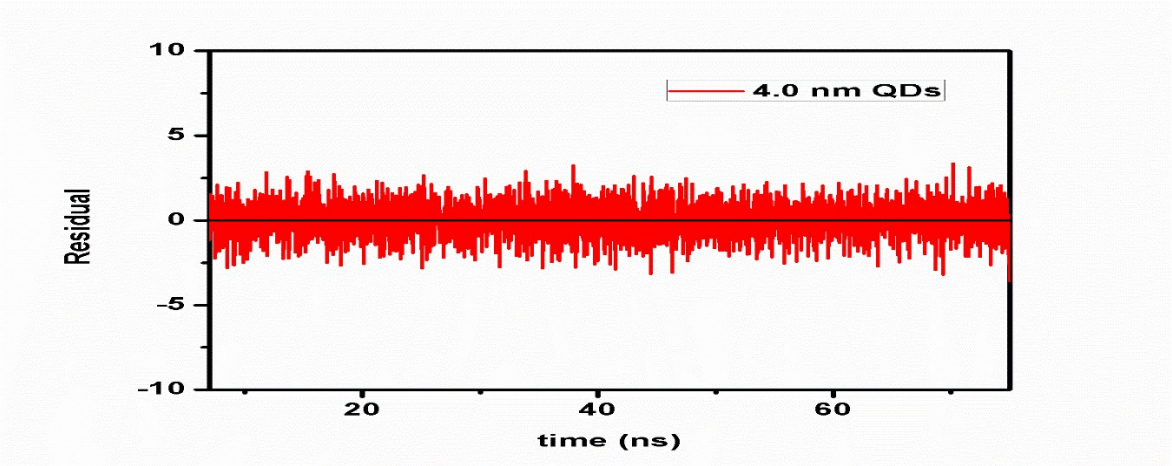


Fig. S6 Time-resolved fluorescence decay curves of Ox170:QDs (a) 3.5 nm CdS, (b) 4.0 nm CdS, and (c) 4.4 nm CdS QDs. Black lines are fitting to the decay curves. Legend shows dye:QD ratios in terms of molar concentration. (Samples excited at 375 nm and emission monitored at donor's emission maximum). The stoichiometry and absolute concentration of Ox170 are given in supporting information.


3.5nm QDs + Ox170
Residual
time (ns)
10
5
0
-5
-10
20
40
60


3.5 nm QDs
Residual
time (ns)
10
5
0
-5
-10
20
40
60


4.0 nm QDs
Residual
time (ns)
10
5
0
-5
-10
20
40
60

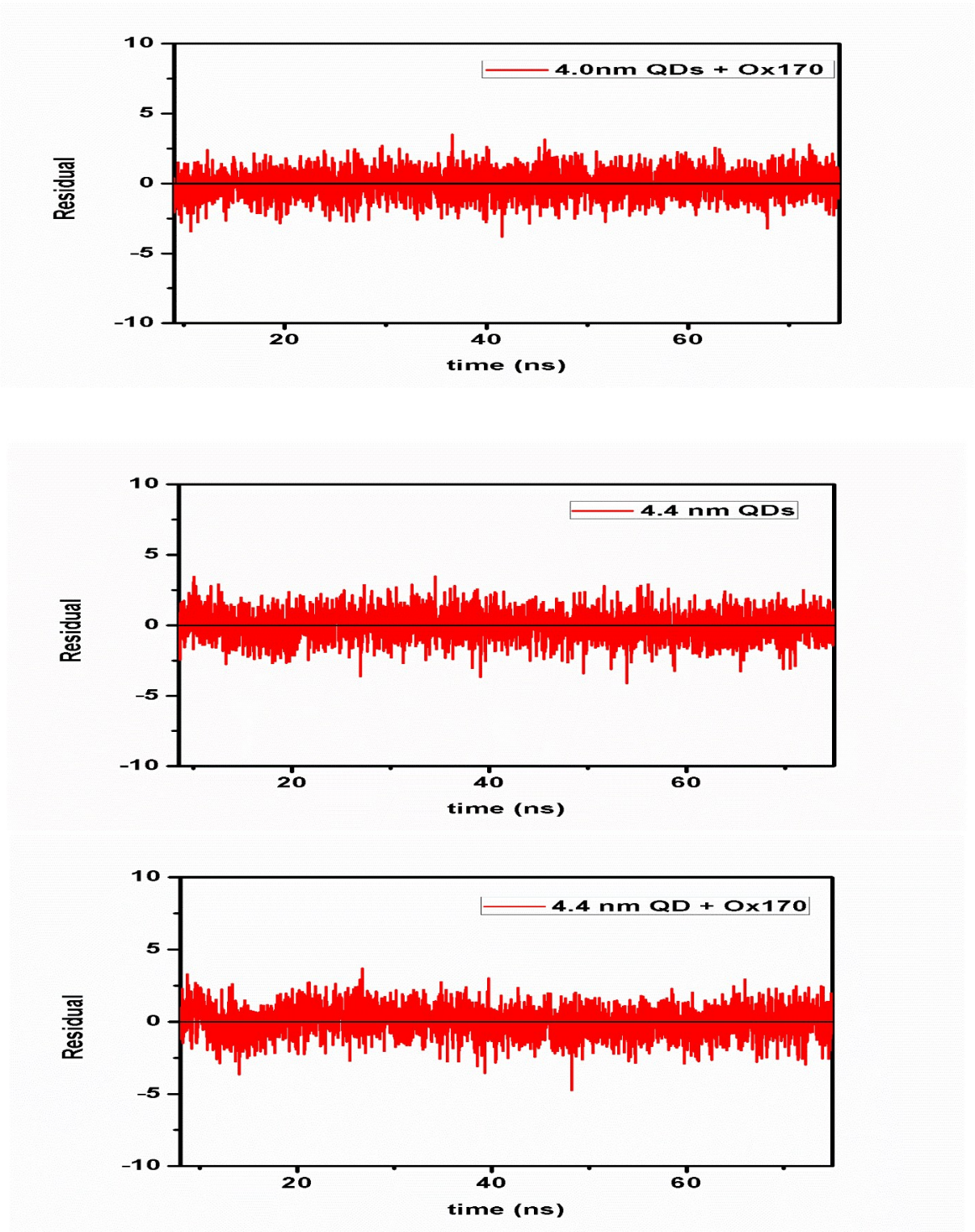


Fig. S7 Residual plots of the tri-exponential fit

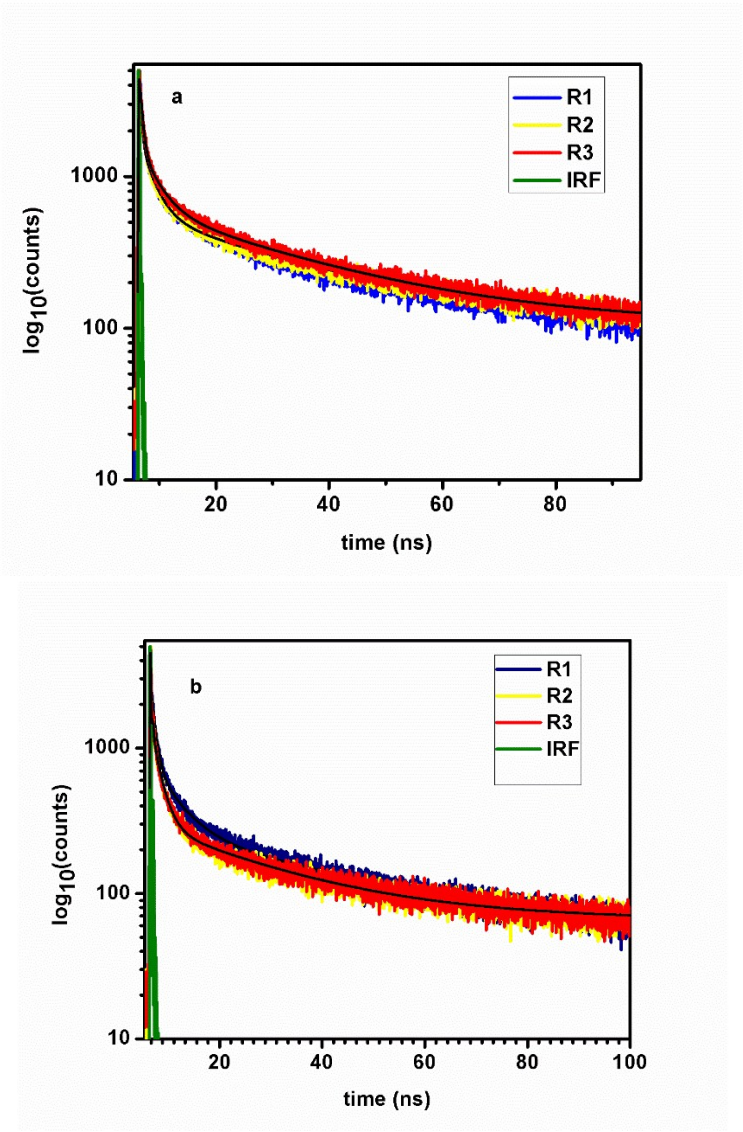


Fig. S8 Time-resolved fluorescence decay curves of 4.4 nm QDs (a) in absence (b) in presence of Ox170. Black lines are fitting to the decay curves.

Table S2 Decay parameters of 4.4 nm QDs (λ_{ex}=375 nm)

No. of repeats	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	α_1	α_2	α_3	$<\tau>$(ns)[a]	$\chi 2$
R1	0.38	2.67	27.51	0.72	0.19	0.09	3.26	1.03
R2	0.31	5.25	51.47	0.85	0.10	0.05	3.36	1.15
R3	0.25	4.14	35.59	0.70	0.24	0.06	3.30	1.16

[a]Experimental error ±5%

Table S3 Decay parameters of 4.4 nm QDs in presence of Ox170 (λ_{ex}=375 nm)

No. of repeats	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	α_1	α_2	α_3	$<\tau>$(ns)[a]	$\chi 2$
R1	0.08	1.83	32.36	0.87	0.11	0.02	0.92	1.05
R2	0.20	1.23	25.04	0.80	0.18	0.02	0.88	1.17
R3	0.18	3.75	34.14	0.86	0.13	0.01	0.98	1.33

[a]Experimental error ±5%

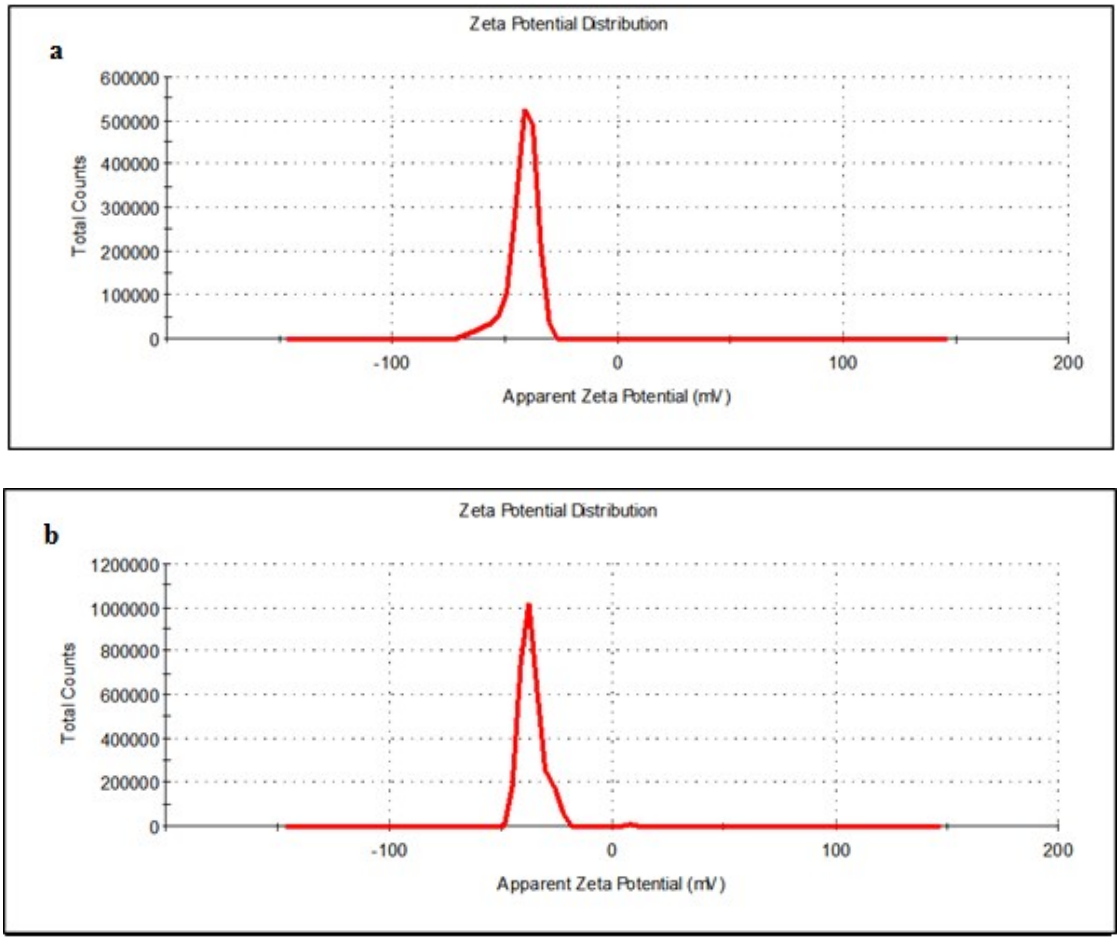


Fig. S9 Zeta potential plots of (a) 3.5 nm CdS, (b) 4.0 nm CdS, QDs.

Preparation of DAET capped CdS QDs: DAET capped CdS nanocrystals were synthesized at room temperature in water with 2-(*N*,*N*-dimethylamino)ethanethiol hydrochloride (DAET) as a colloidal stabilizer.[1] Deionized water was sparged with ultrahigh purity argon for 60 min. To 150 mL of the argon sparged water was added 27.5 mg of CdCl2 (0.15 mM) along with 398 mg of tertiary amine thiol (3.5 mM). The pH of this clear mixture was adjusted to 7.0 by dropwise addition of 1 M NaOH. In a separate flask, 60 mg (0.25 mM) of Na_2S was dissolved in 25 mL of argon sparged water and transferred dropwise to the cadmium chloride solution. The solution turned pale yellow immediately after sulfide addition.The formed QDs were centrifuged and washed with adding ethanol to remove unreacted ions. These QDs were again resuspended in deionised water.Thereafter, UV Vis spectra and zeta potential are measured to check the stability of the QDs. (Fig. S10)

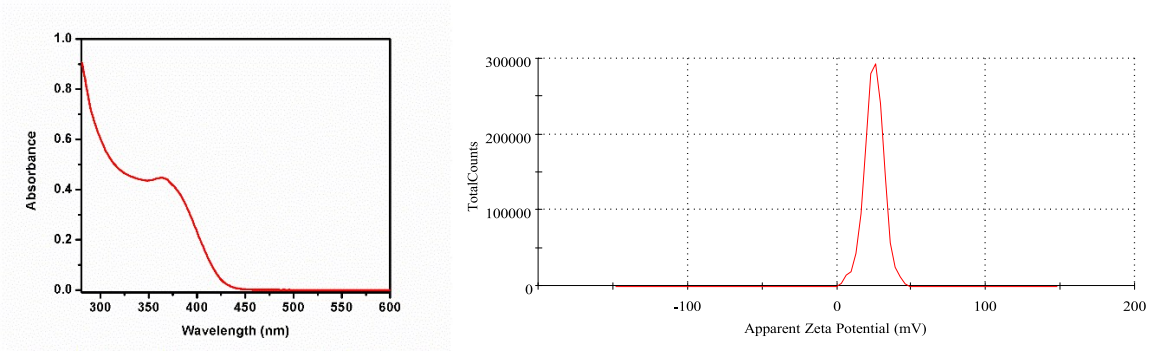


Fig. S10 Absorption spectra and zeta potential plot (ζ= +24.9mV) of DAET capped CdS QDs

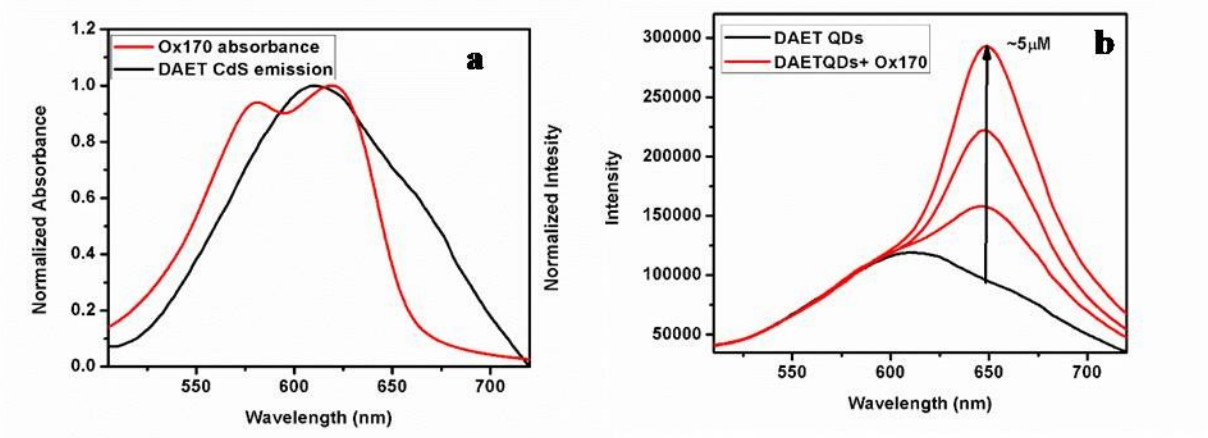


Fig. S11 (a) Spectral overlap between DAET capped CdS QDsand Ox170 (b)Emission of DAET capped CdS QDs in presence of Ox170 at different concentration (e.g. 1µM, 3µM, 5µM), excited at 375nm.

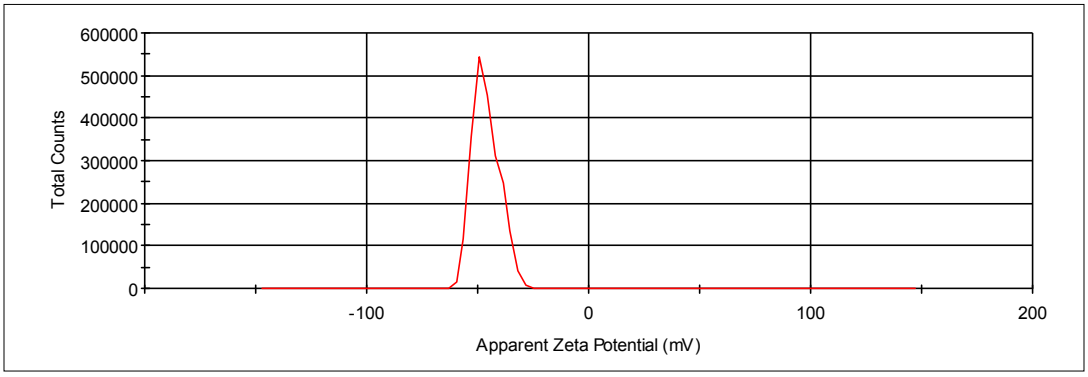


Fig. S12 Zeta potential (-41.7 mV) plots of 4.4 nm QDs in presence of Ox170

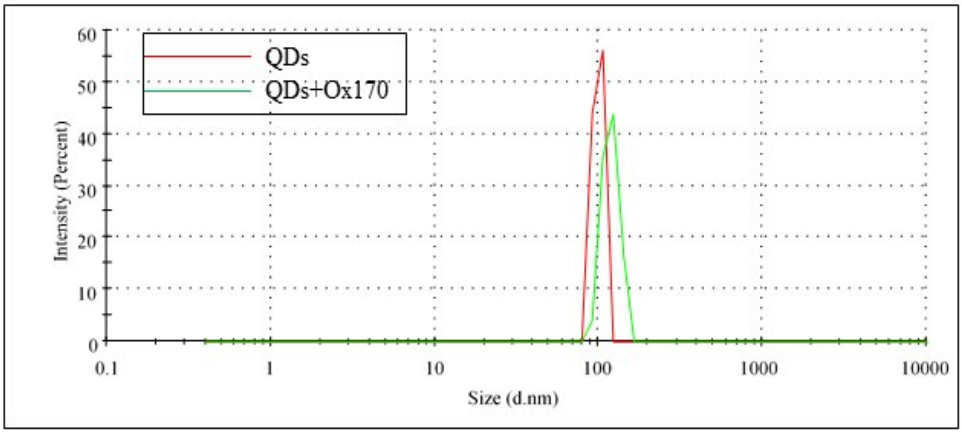


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Fig. S13 DLS plot of 3.0 nm CdS QDs in absence and in presence of Ox170

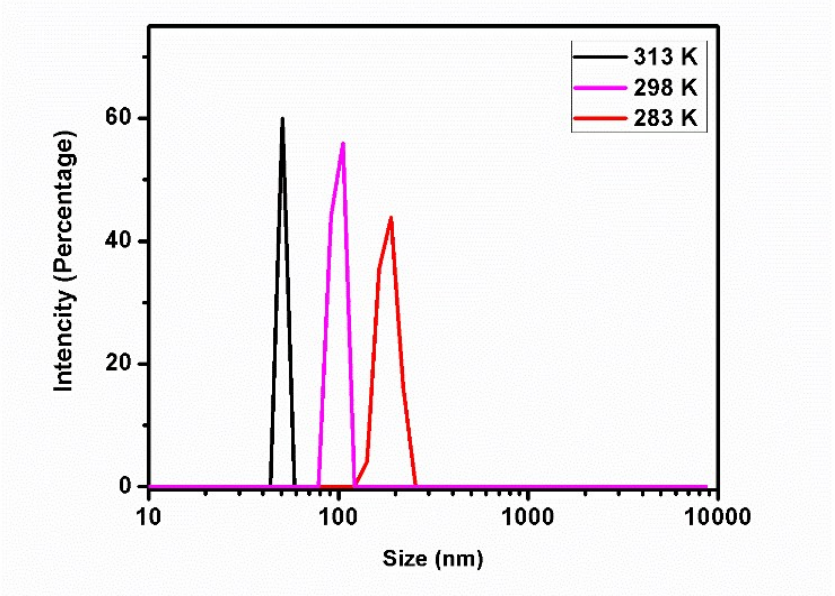

Fig. S14 DLS plot of 3.0 nm CdS QDs at 313K (size~190 nm), 298K (size~99.4 nm), 283K (size~50.7 nm)

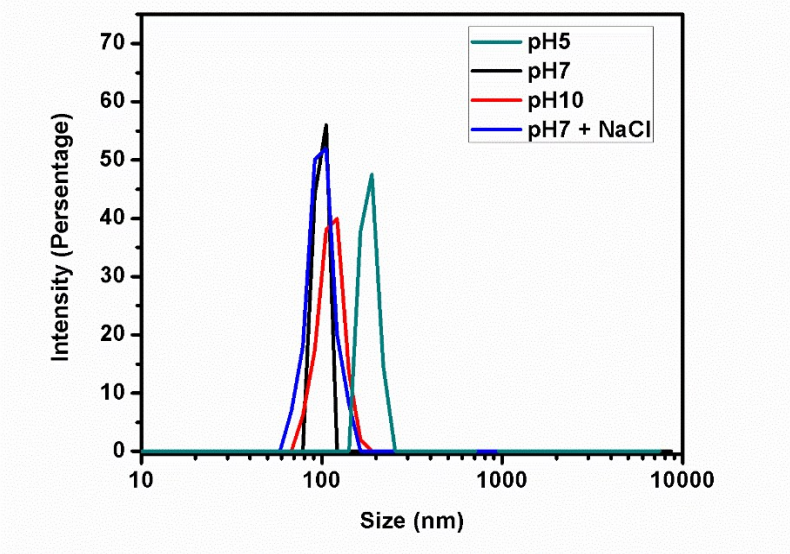

Fig. S15 DLS plot of 3.0 nm CdS QDs at pH 5 (size~182.2 nm), pH7 (size~99.4 nm), pH10 (size~122.8 nm) and with NaCl (91.3 nm).

Reference

(1) M. Warrier, M. K. F. Lo, H. Monbouquette and M. A. Garcia-Garibay, *Photochem. Photobiol. Sci.*, 2004, **3**, 859.