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Title:	"Giant" Multishell CdSe Nanocrystal Quantum Dots With Suppressed Blinking
Author(s):	Yongfen Chen, Javier Vela, Han Htoon, Joanna L. Casson, Donald J. Werder, David A. Bussian, Victor I. Klimov, and Jennifer A. Hollingsworth*
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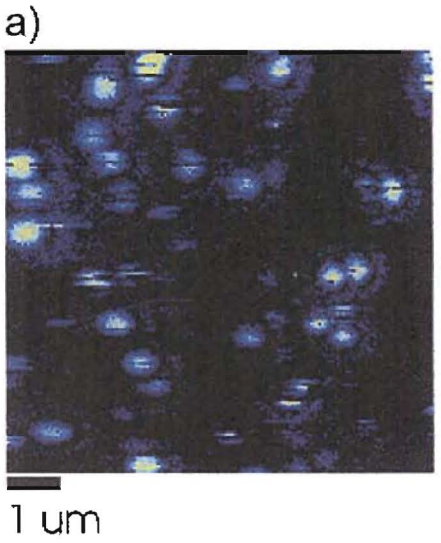
"Giant" Multishell CdSe Nanocrystal Quantum Dots With Suppressed Blinking

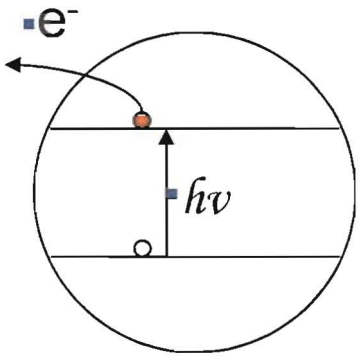
Yongfen Chen, **Javier Vela**, Han Htoon, Joanna L. Casson, Donald J. Werder, David A. Bussian, Victor I. Klimov, and Jennifer A. Hollingsworth*

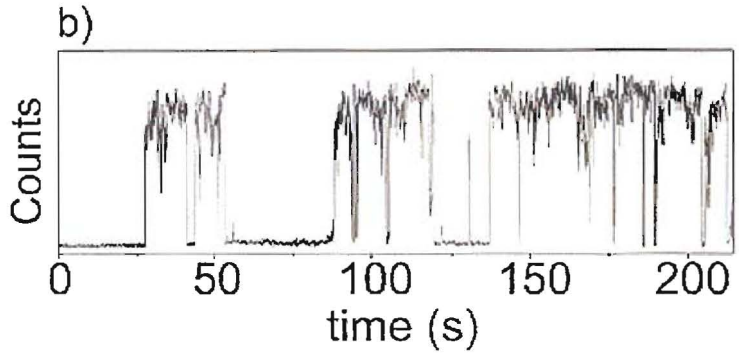
Chemistry Division and Center for Integrated Nanotechnologies
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

236th ACS Fall National Meeting, Philadelphia, PA

Fluorescence Intermittency of Single CdSe QDs

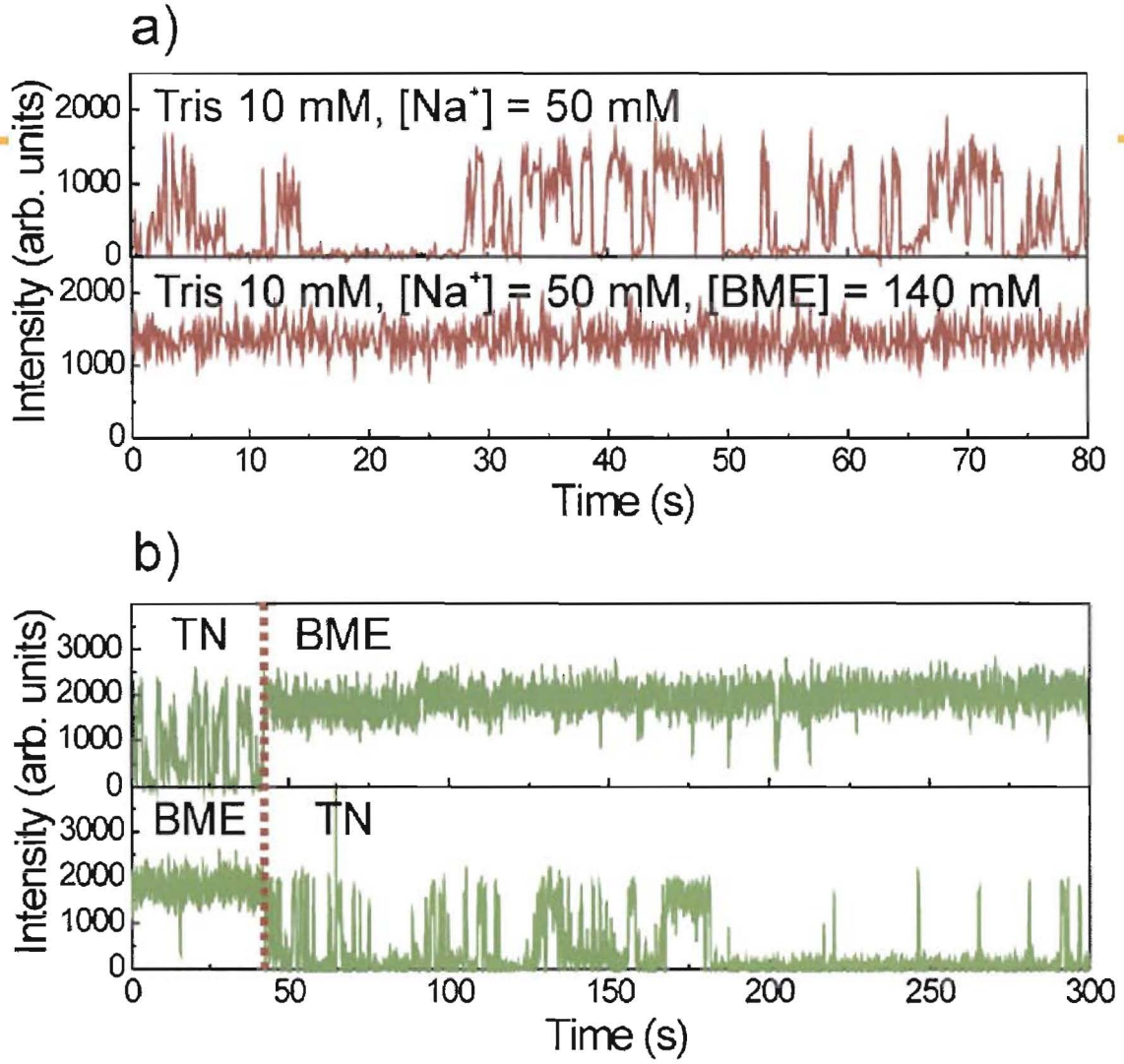






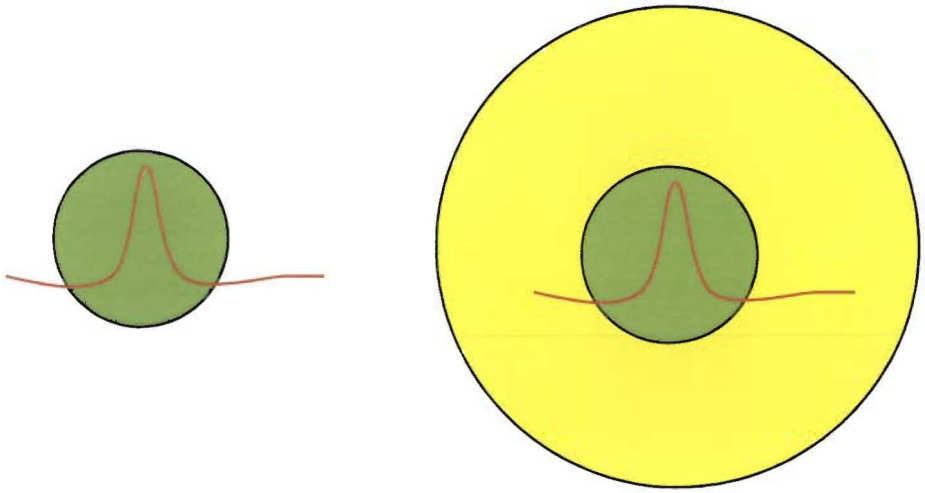
- Nirmal, M.; B.O.Dabbousi, M. G. Bawendi, J.J. Macklin, J. K. Trautman, T. D. Harris, L. E. Brus. *Nature*. **1996**; 383.802-804.

- Way to suppress blinking

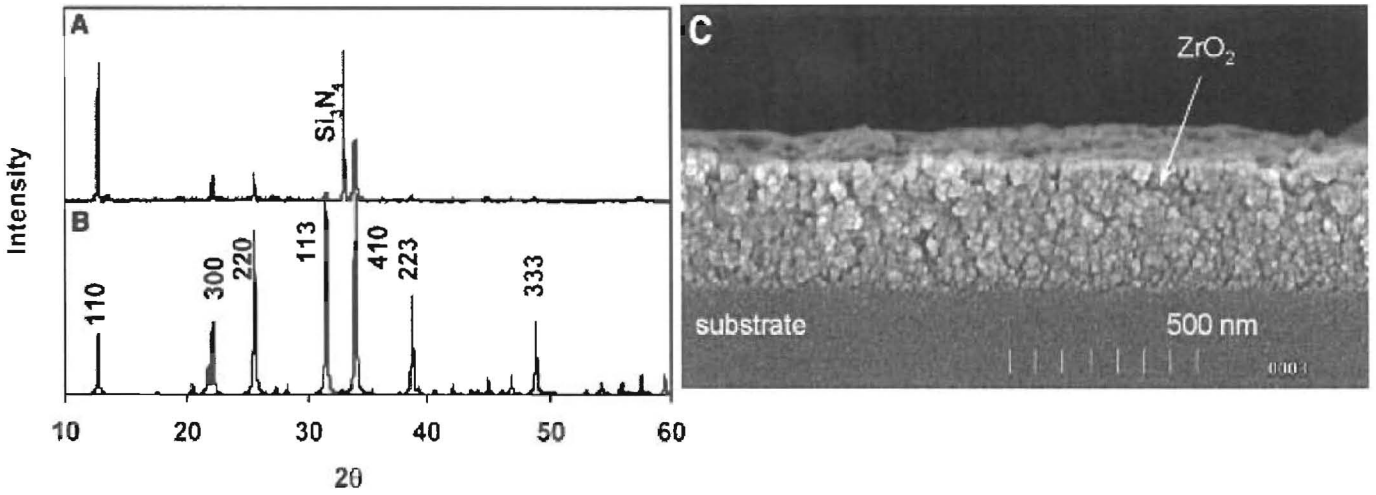


- Hohng, S.; Ha, T. *J. Am. Chem. Soc.*; **2004**; 126(5); 1324-1325

▪Complete confinement of wavefunction in a thick shell



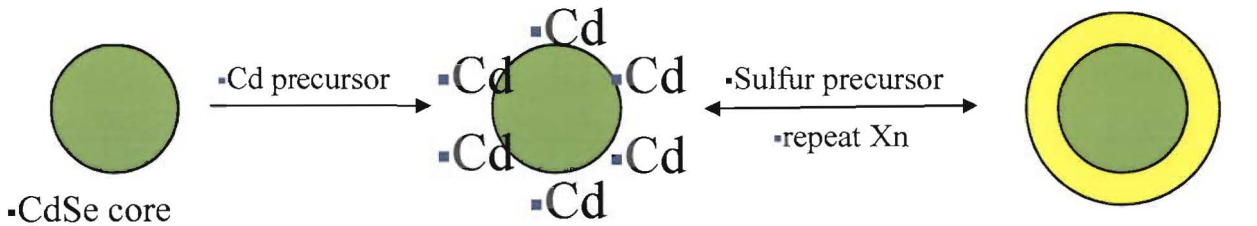
▪Original Succesive Ionic Layer Adsorption and Reaction (SILAR) for thin film prepration



▪(A) X-ray diffraction pattern of Zn2SiO4 film on Si3N4/Si. (B) Simulated powder x-ray diffraction pattern of Zn2SiO4. (C) Electron micrograph of ZrO2 film on Si3N4/Si substrate.

▪Sangmoon Park, Benjamin L. Clark, Douglas A. Keszler, Jeffrey P. Bender, John F. Wager, Thomas A. Reynolds, and Gregory S. Herman. **Low-Temperature Thin-Film Deposition and Crystallization** *Science* **2002** 297, 65

▪Modified SILAR method for Multishell CdS growth

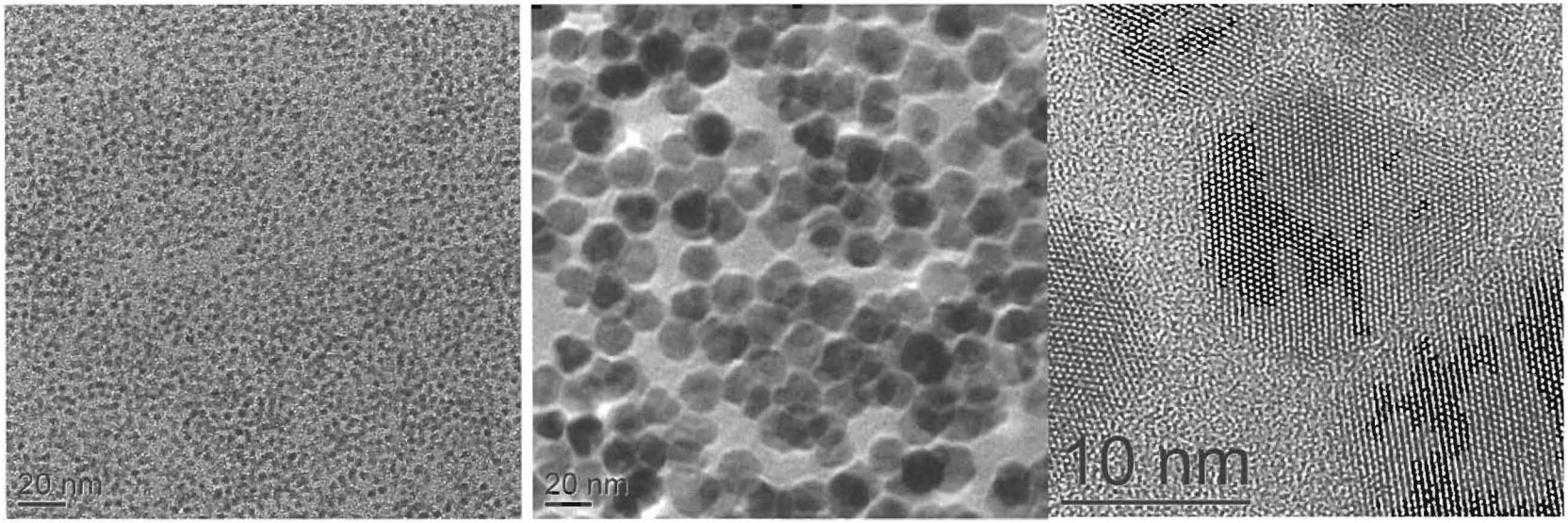


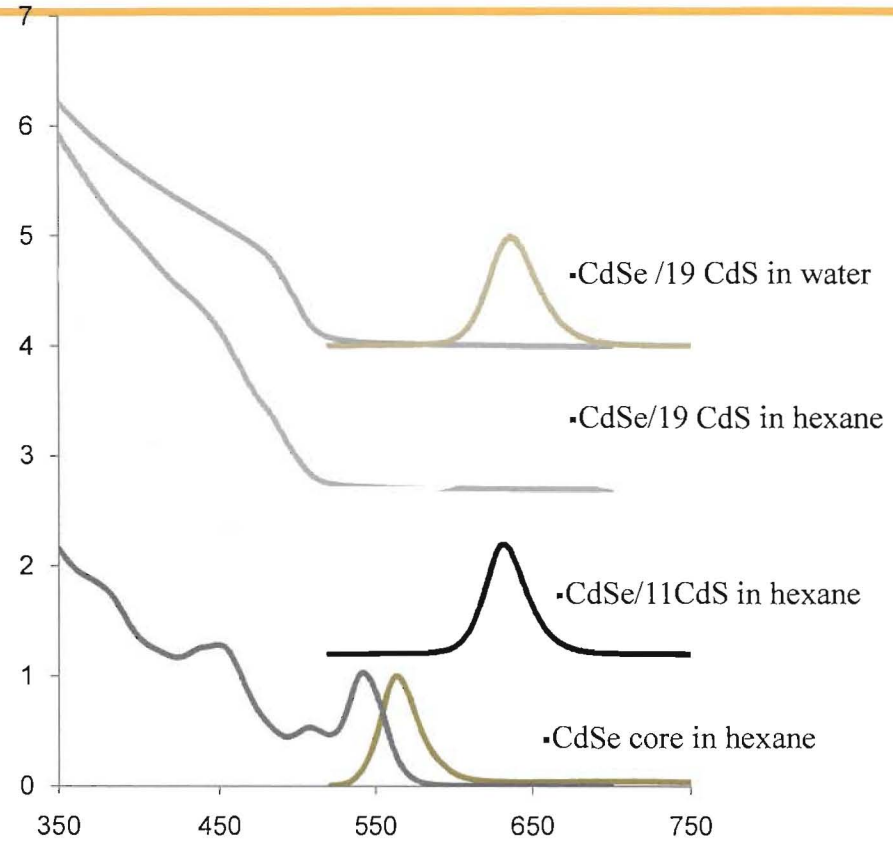
▪CdSe core

▪With Se rich surface

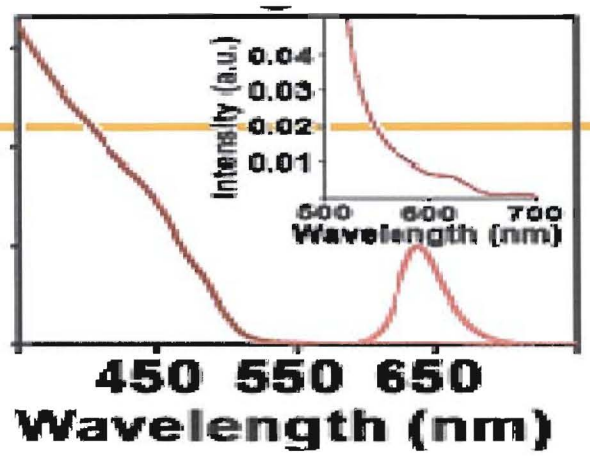
▪CdSe/n CdS shell

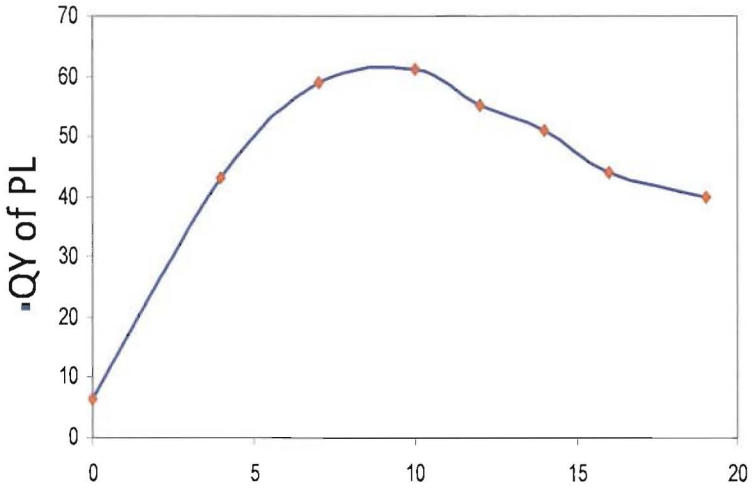
▪Li, J. J.; Wang, Y. A.; Guo, W.; Keay, J. C.; Mishima, T. D.; Johnson, M. B.; Peng, X. J. Am. Chem. Soc; **2003**; 125(41); 12567-12575


20 nm
20 nm
10 nm



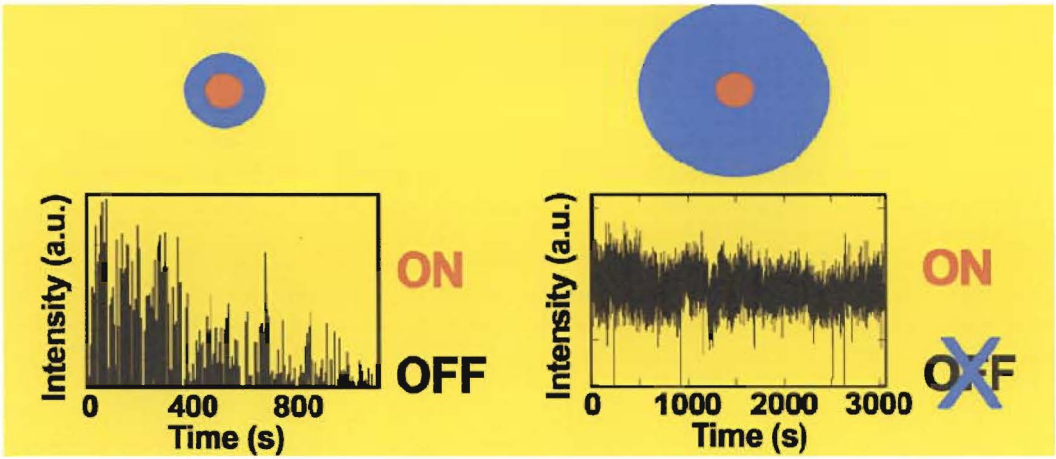
▪Wave length (nm)





▪Number of CdS monolayer

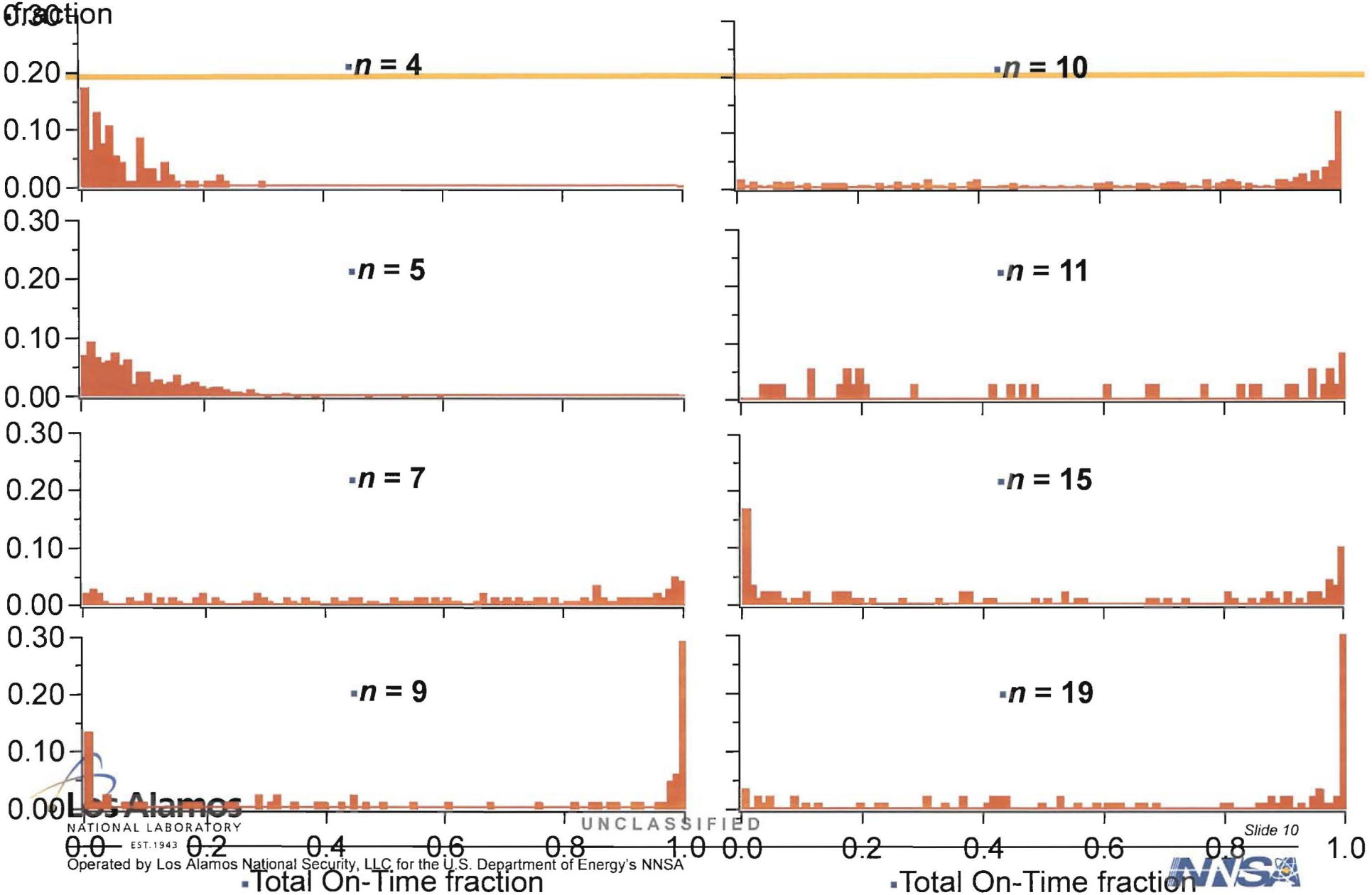
"Giant" Multishell CdSe Nanocrystal Quantum Dots With Suppressed Blinking



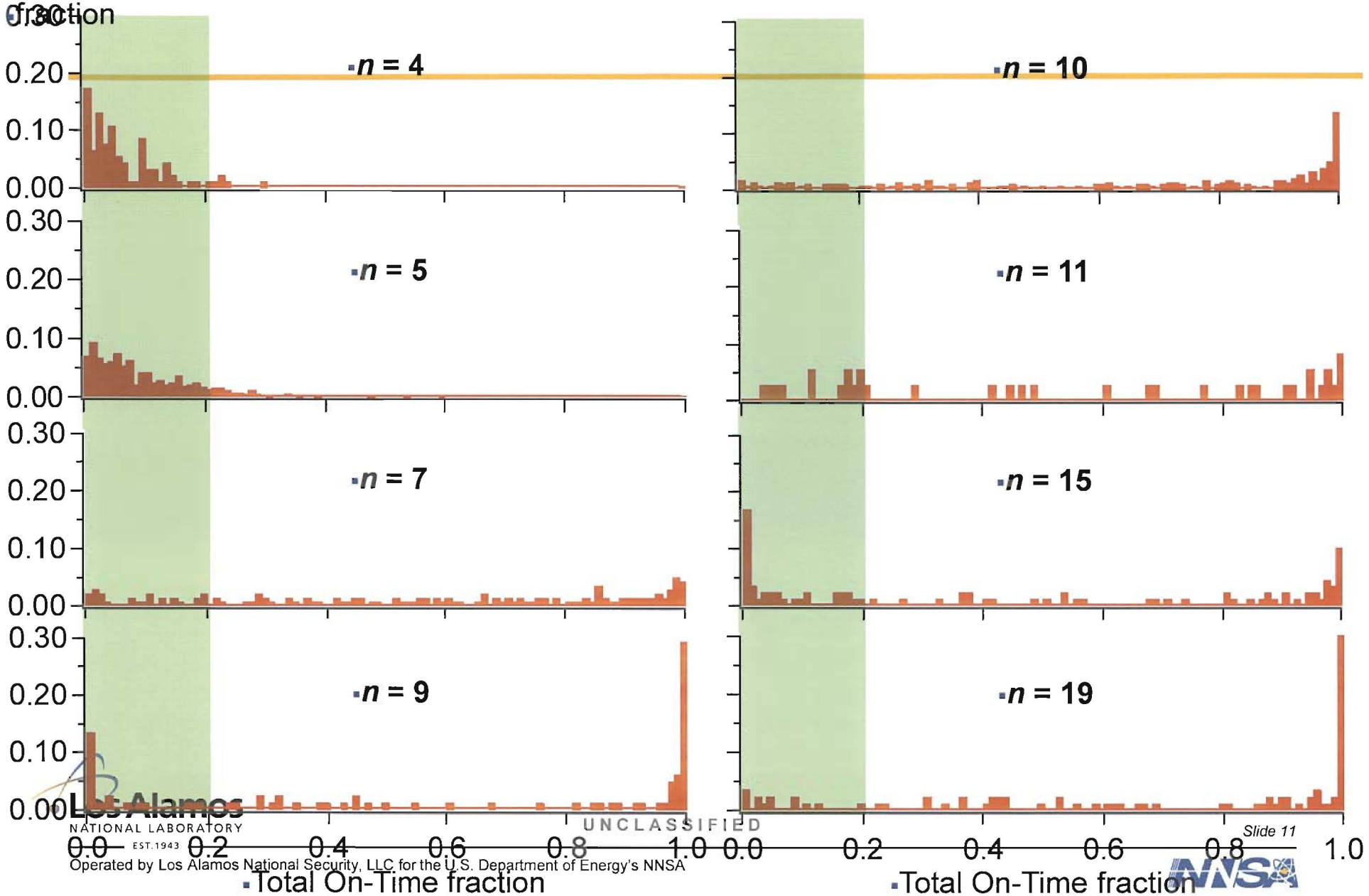
- Chen et al. *JACS* **2008**, *130*, 5026

- All blinking experiments:
- λ_{exc} = 532 nm, 180 mW
- 54 min runs (total time)
- 200 ms binning (acq & read-out 100 ms each)

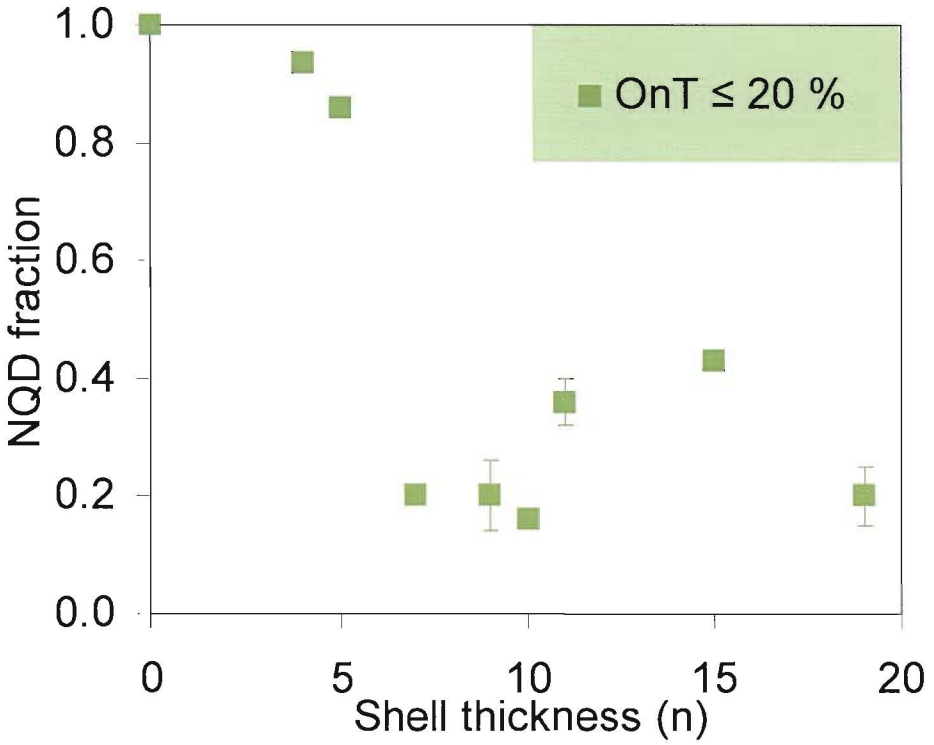
CdSe/*n*CdS: Blinking behavior over time



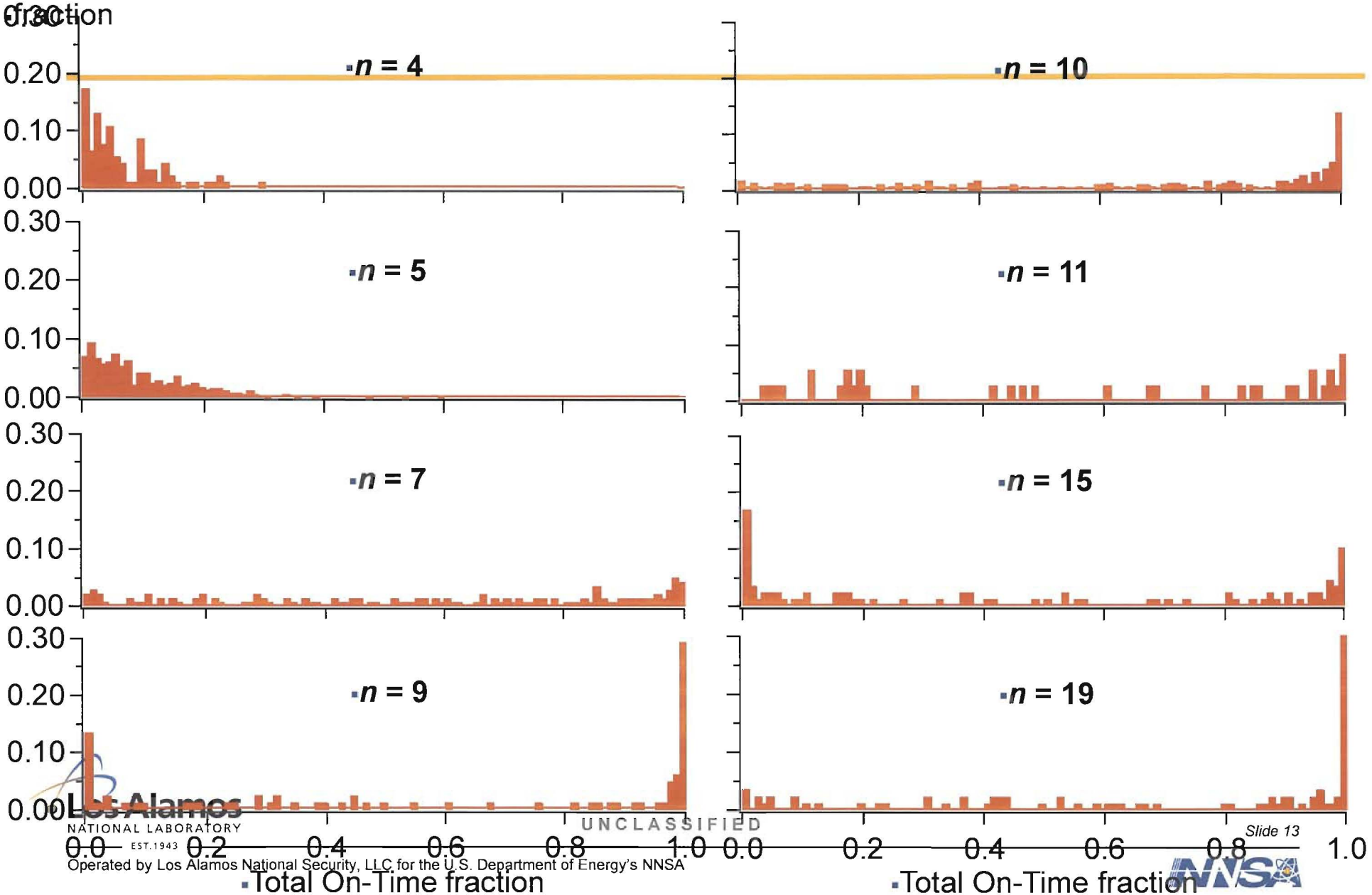
CdSe/*n*CdS: Blinking behavior over time



Blinking behavior vs. shell thickness (n)

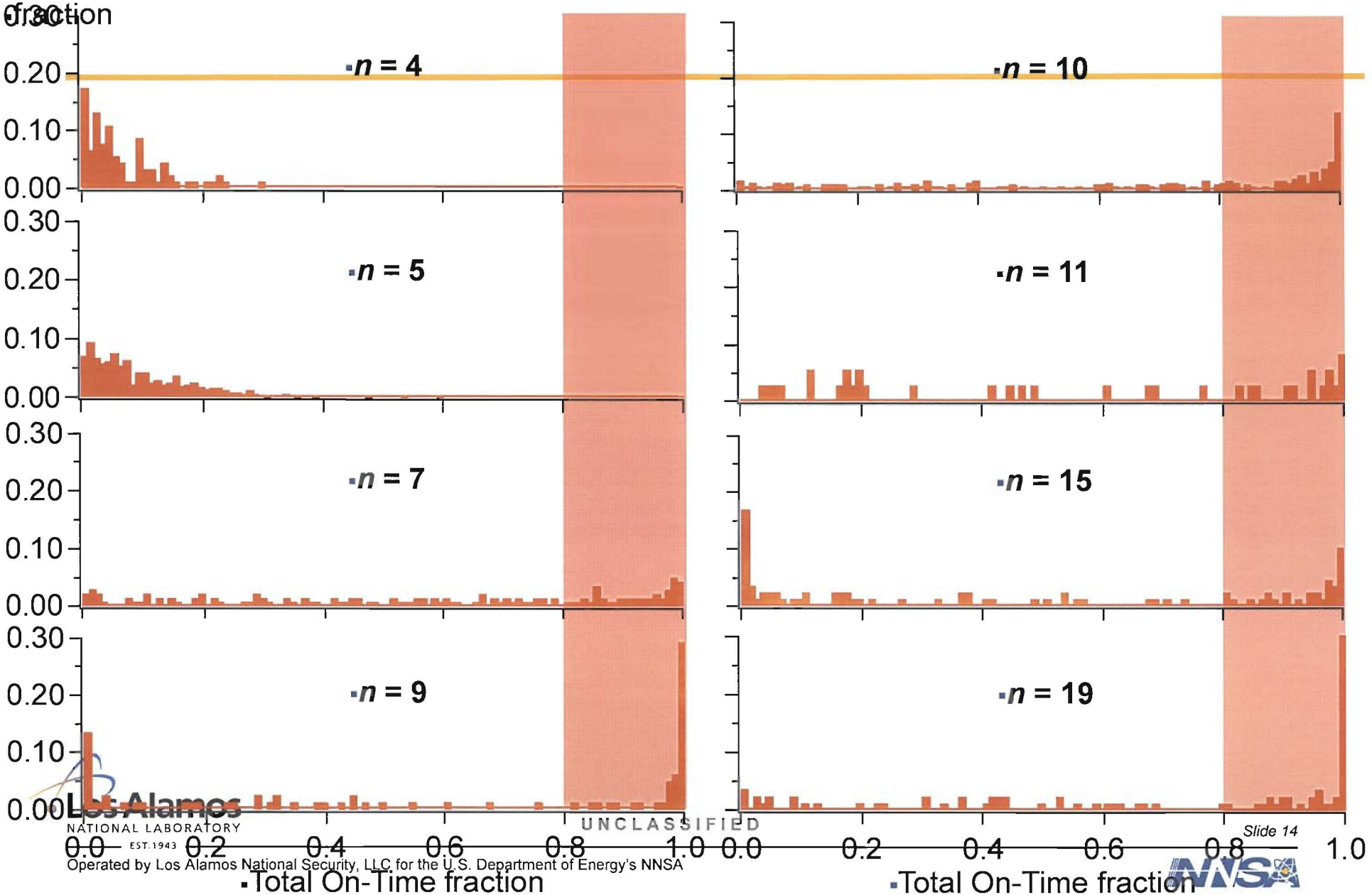


CdSe/*n*CdS: Blinking behavior over time

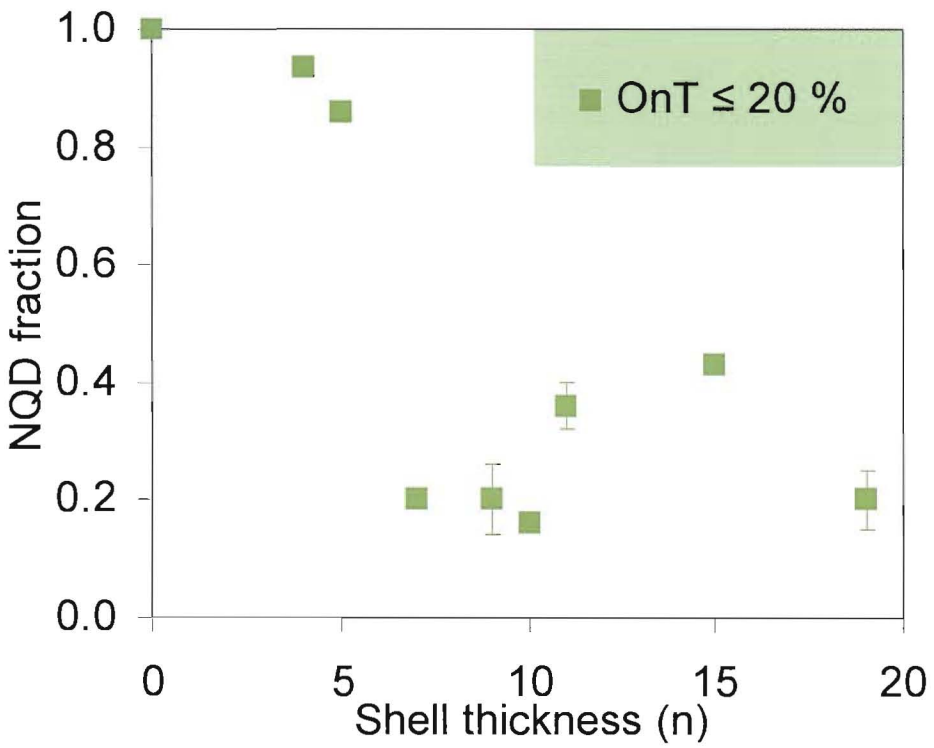


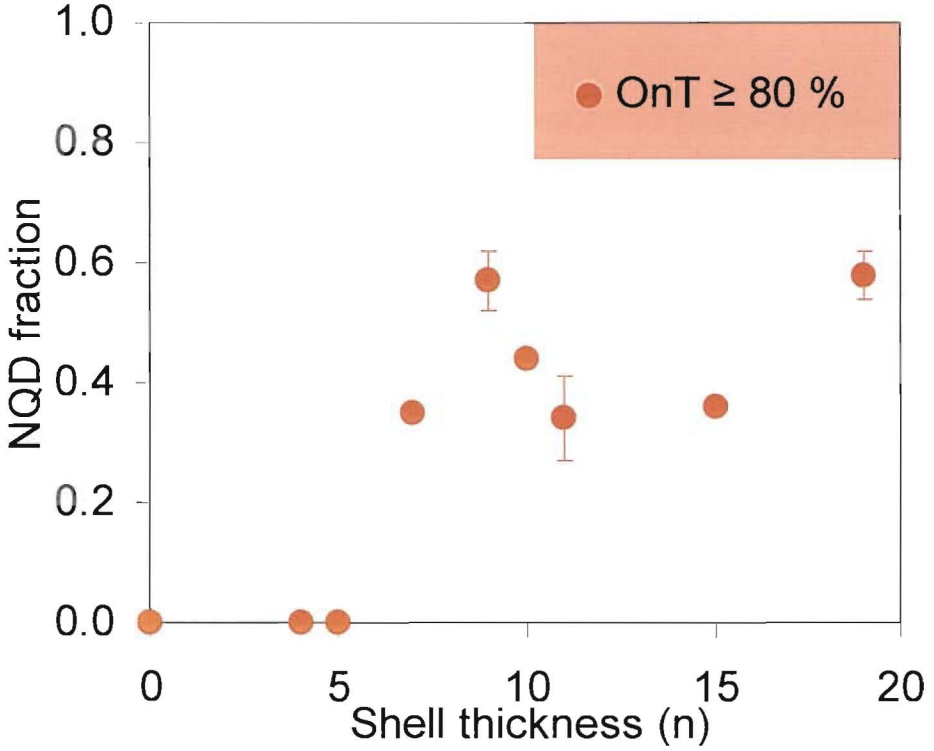
▪CdSe/*n*CdS: Blinking behavior over time

▪NQD



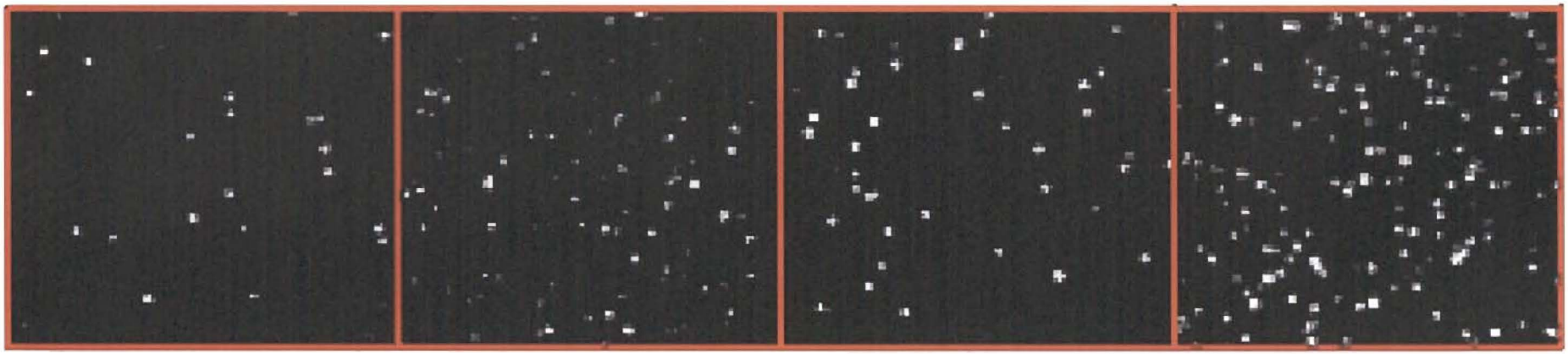
Blinking behavior vs. shell thickness (n)





Gdot blinking: How does it look like?

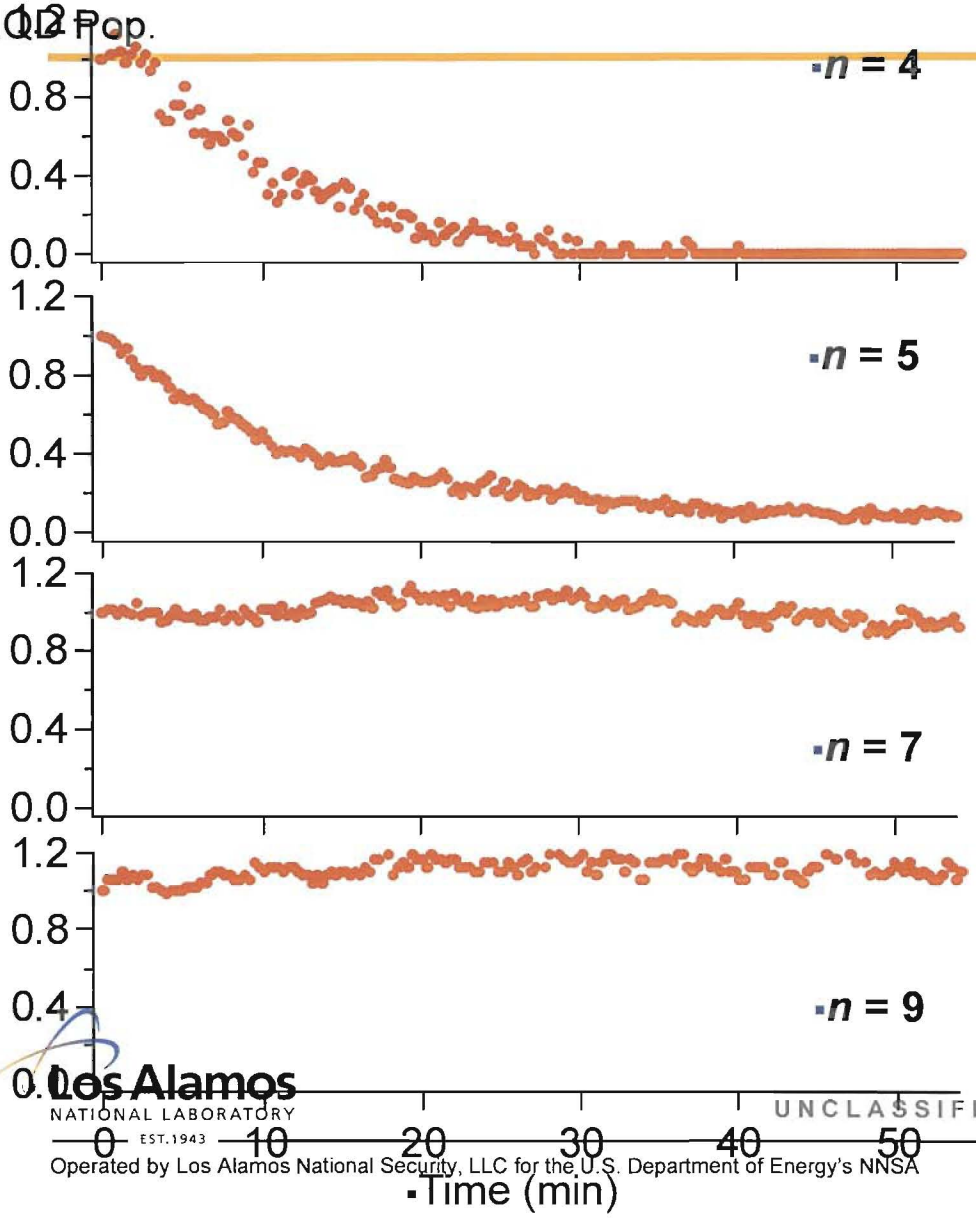
- CdSe/4CdS
- CdSe/7CdS
- CdSe/9CdS
- CdSe/19CdS



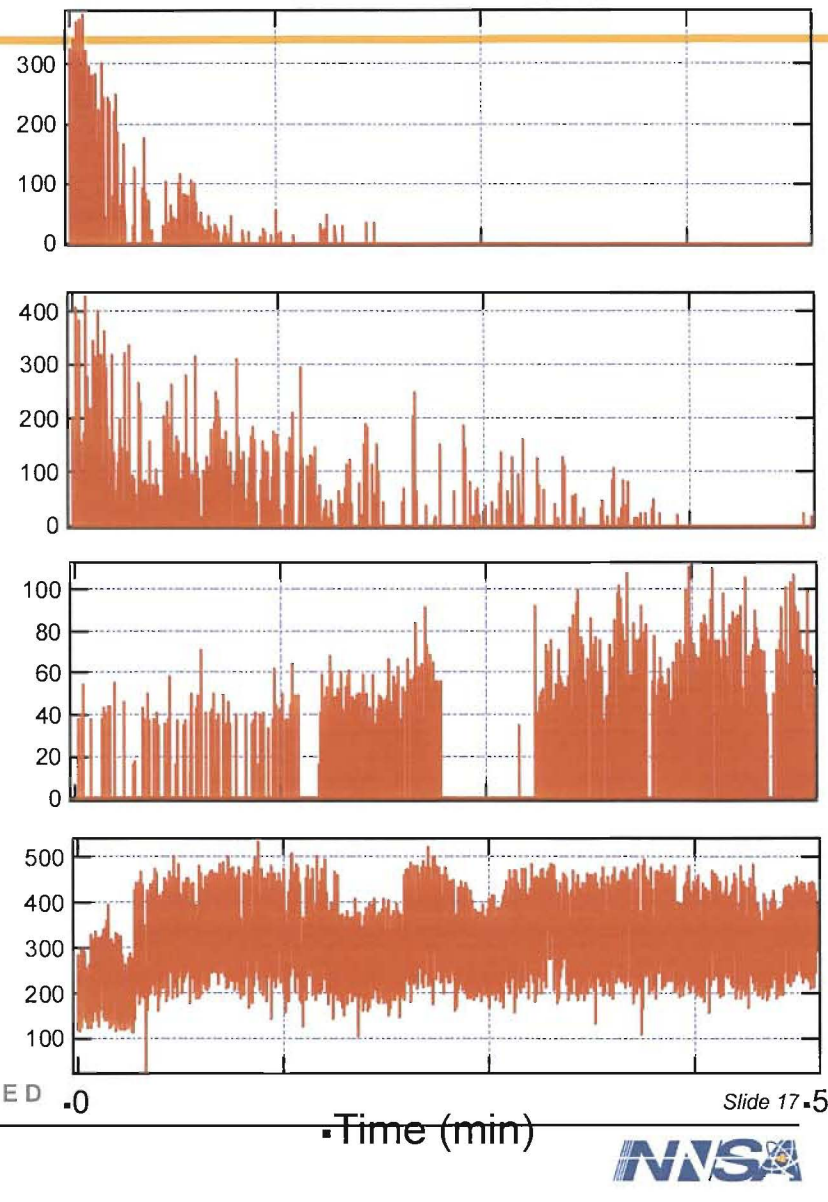
▪CdSe/*n*CdS: Photostability

▪Normalized

▪NQD Pop.



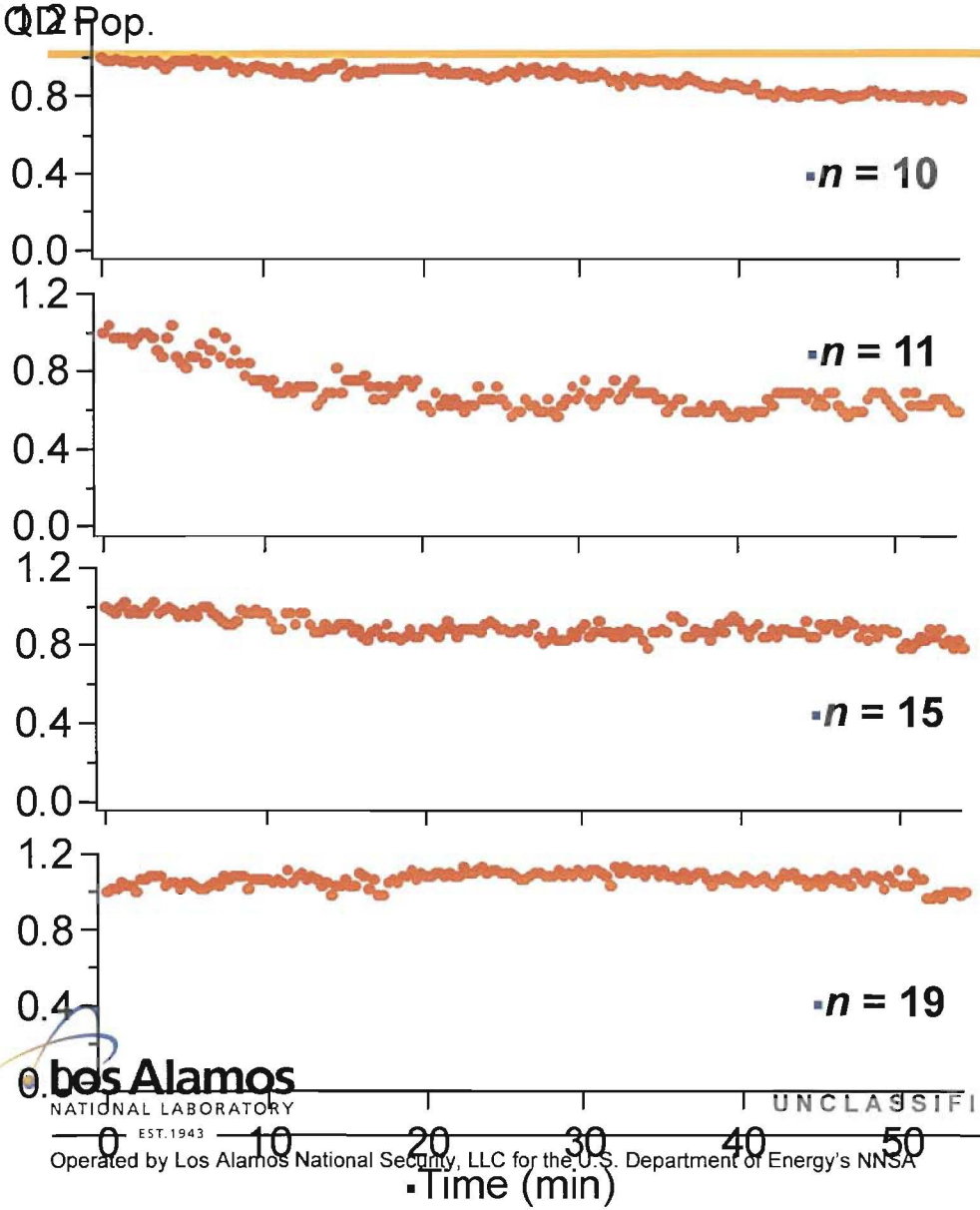
▪Sample trace



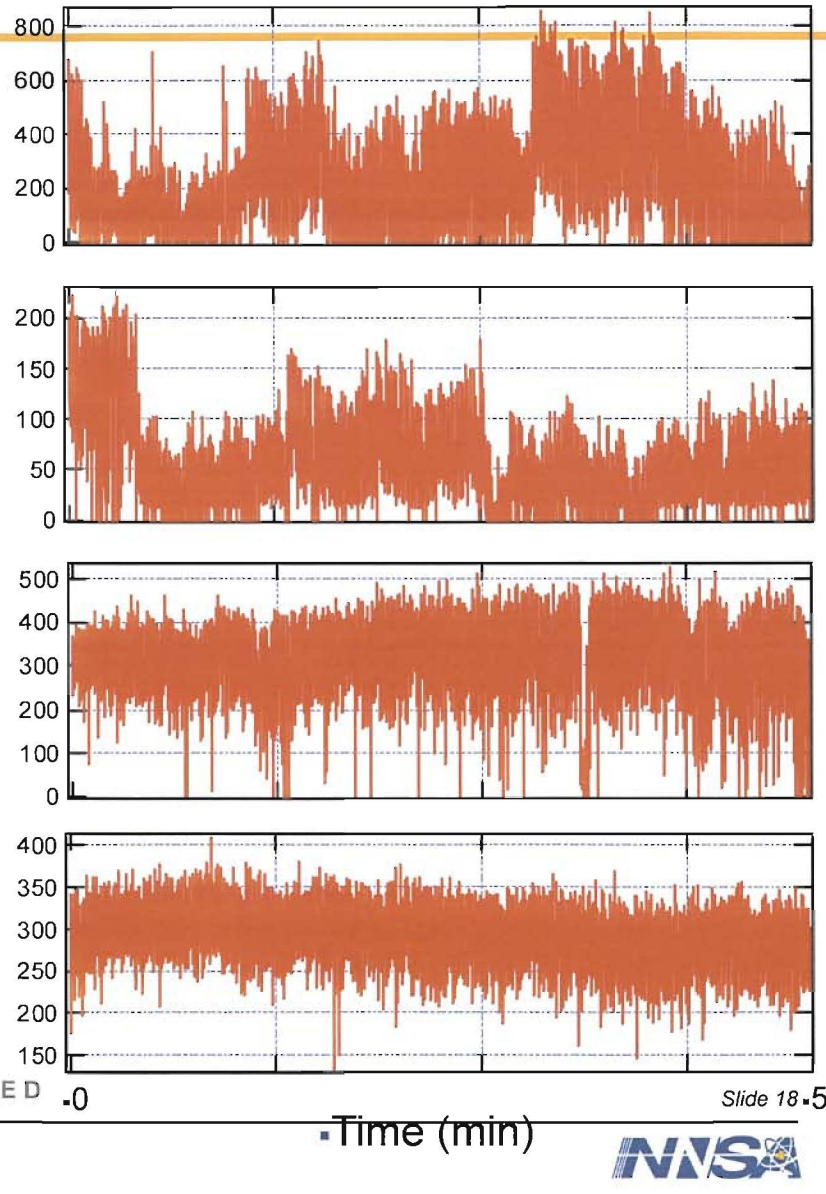
▪CdSe/*n*CdS: Photostability

▪Normalized

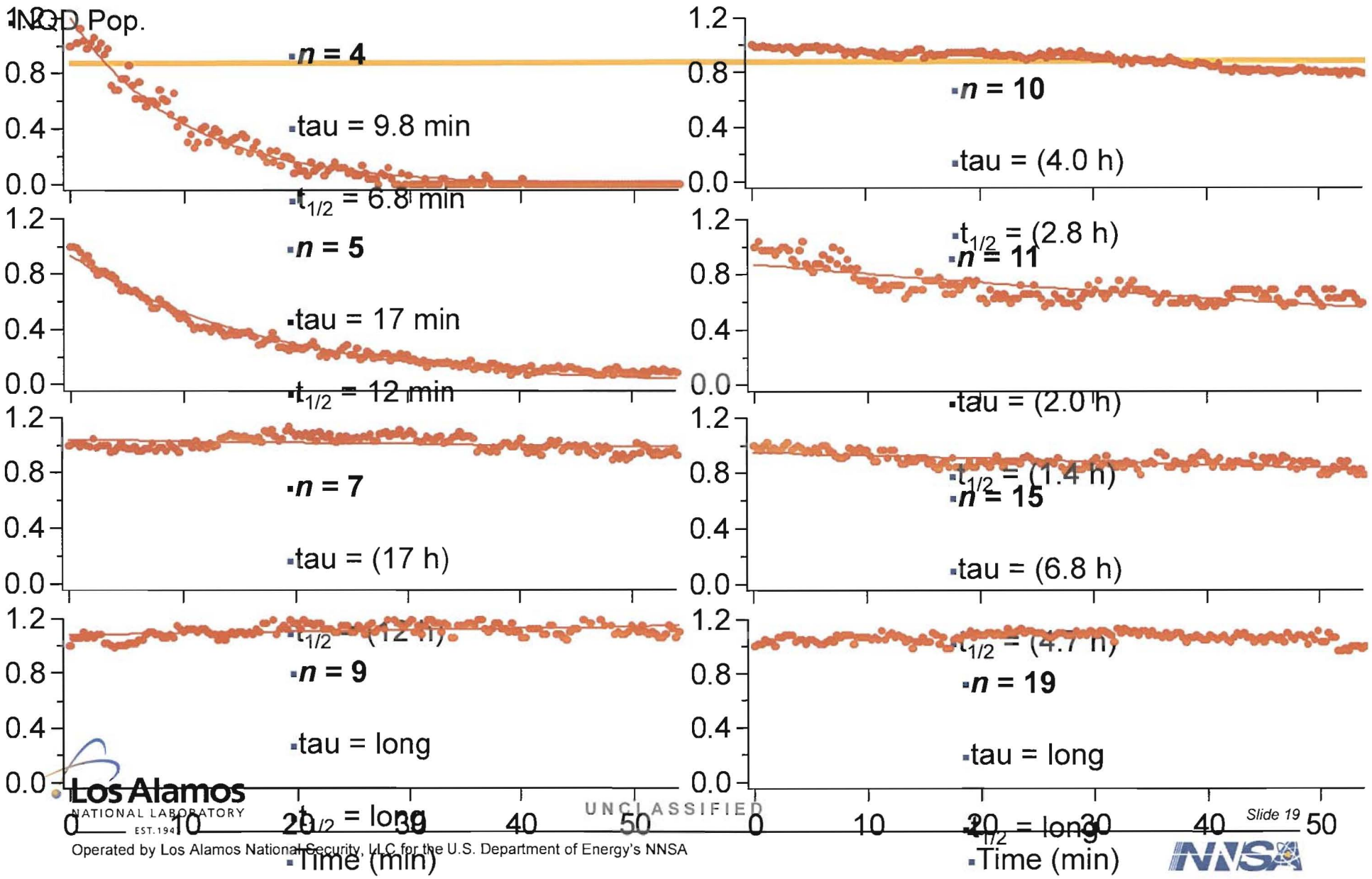
▪NQD Pop.



▪Sample trace



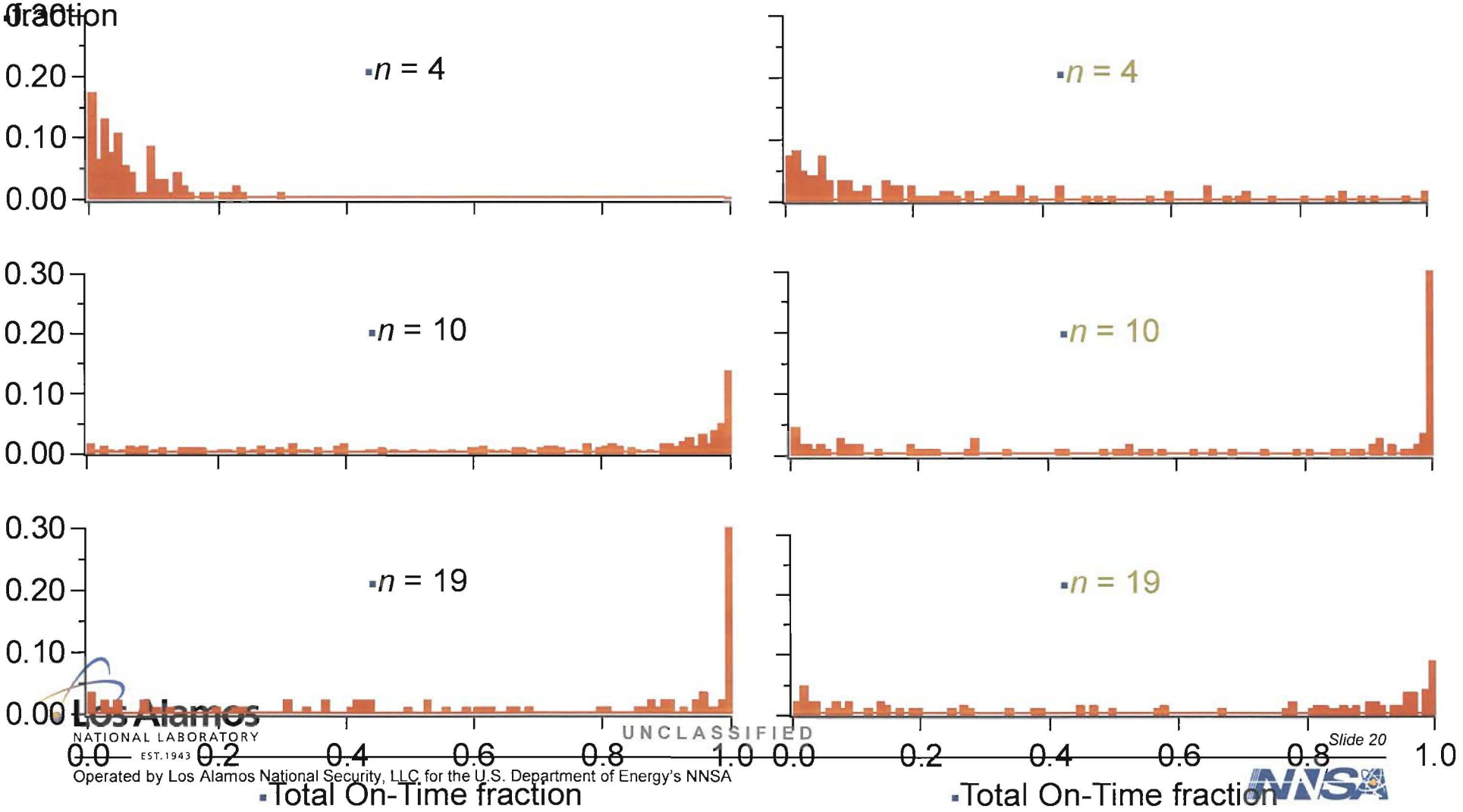
CdSe/*n*CdS: Photostability



CdSe/*n*CdS: Blinking behavior vs. ligand & solvent

- Gdot-npL / hexane $\xrightarrow[+\ Me_3NH^+OH^-\ /\ de\text{-}water]{MSAH_2\ (HOOCCH_2CH(SH)COOH)}$ Gdot-MSA / water

- NQD



CdSe/*n*CdS: Blinking behavior vs. ligand & solvent

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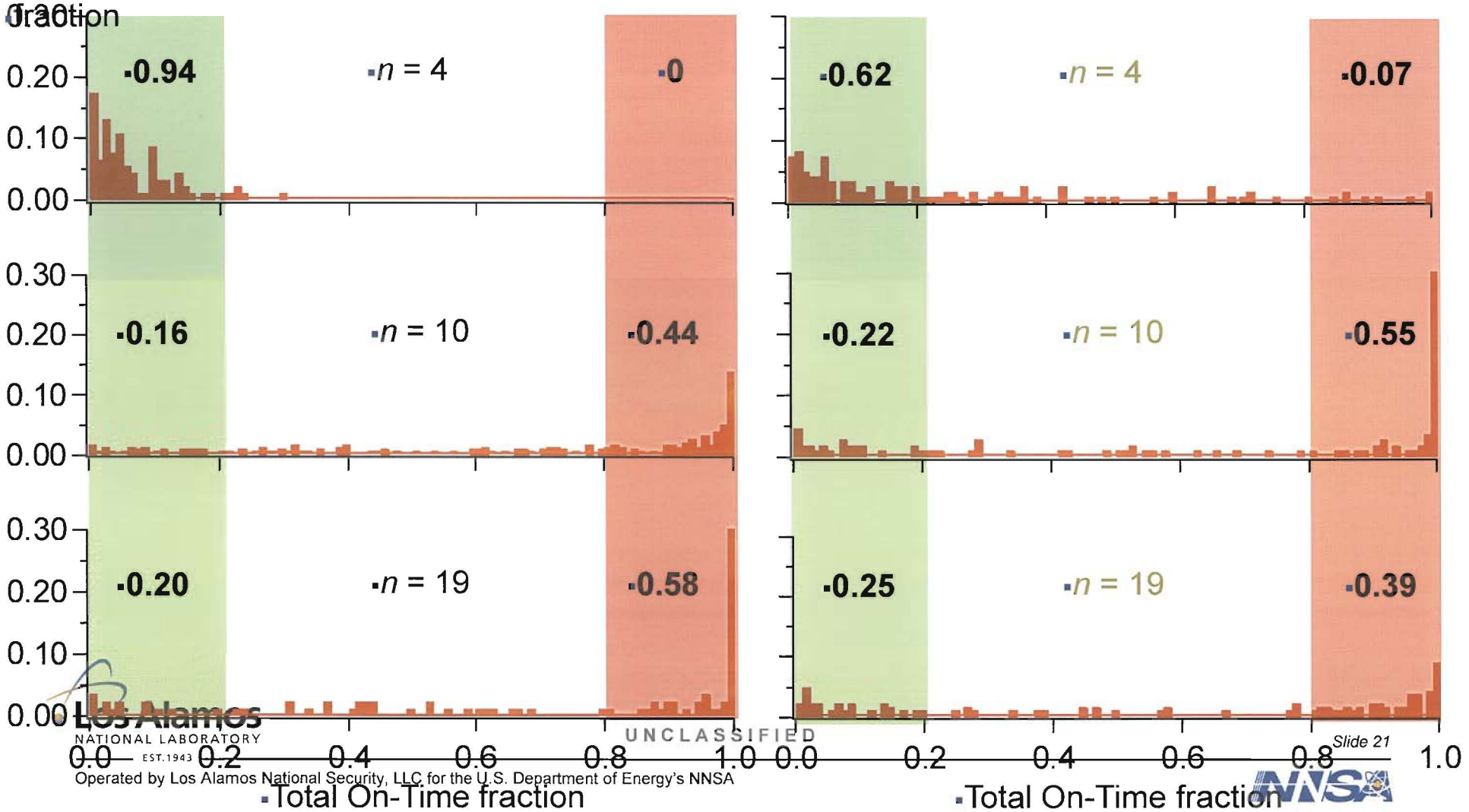

Blinking behavior of other samples

- Different preps/conditions
- (Useful tool for chemistry improvement!)

Sample	OT ≥ 80 %	OT ≤ 20 %
CdSe/18CdS-**oleylamine**	13 %	39 %
CdSe/14CdS-**TOPO-'amine'**	0	75 %
CdSe/19CdS-**TOPO-ODE**	39 %	30 %

- Giant alloys

Sample	OT ≥ 80 %	OT ≤ 20 %
CdSe/**11CdS/6CdZnS/2ZnS**	47 %	13 %
CdSe/**11CdS/6CdZnS/2ZnS**	62 %	15 %
CdSe/**11CdS/6CdZnS/2ZnS**	57 %	13 %
CdSe/**11CdS/6CdZnS/2ZnS**	46 %	20 %
(average of four)	53±8 %	15±3 %

Gdot blinking: Control experiments I

- DLS Analyses of original concentrated solutions (without filtering!)

Table S1. Dynamic light scattering analysis of g-NQDs.

Sample	HD (nm)[a]	PDI (%)	PDI (nm)
CdSe/11CdS/6Cd_xZn_yS/2ZnS	25.1	9.5	2.4
CdSe/11CdS/6Cd_xZn_yS/2ZnS	24.5[b]	9.0	2.2
CdSe/19CdS	23.0	3.2	0.7

[a]HD = Hydrodynamic (total) diameter; measured in toluene or hexane after one or two precipitations with MeOH. HD values are corrected against polystyrene latex standards (20-60 nm). [b]Unwashed: measured in growth solution.

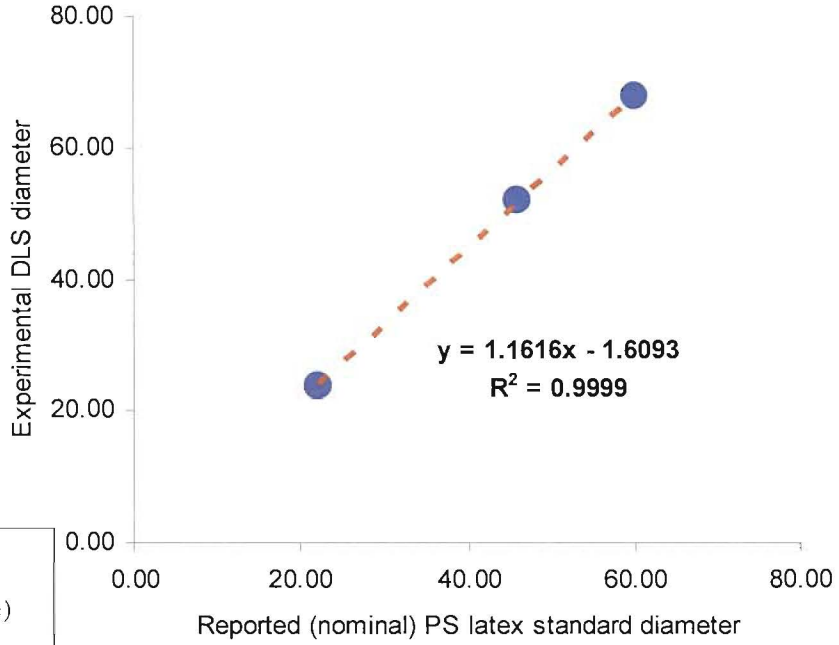

Table S2. Comparison of TEM-derived total size with DLS-derived total size.

sample	TEM total size (from histograms + 2 ligand layers)	DLS total size (HD) (from corrected HD's in Table S1 above)
giant alloy	15.4-21.6 nm	22.7-27.5 nm (washed) 22.3-26.7 nm (unwashed)
giant 19CdS	18.4-24.2 nm	22.3-23.7 nm

- Chen et al. *JACS* **2008**, *130*, 5026

Gdot blinking: Control experiments II

- Concentration (**in**)dependence

Sample	ND	OT ≥ 80 %	OT ≤ 20 %
CdSe/10CdS	54	43 %	17 %
CdSe/10CdS	304	45 %	15 %
CdSe/10CdS-in water	55	62 %	20 %
CdSe/10CdS-in water	111	56 %	23 %
CdSe/11CdS	87	29 %	39 %
CdSe/11CdS	36	39 %	33 %
CdSe/19CdS	315	57 %	22 %
CdSe/19CdS	85	62 %	24 %
CdSe/19CdS-in water	255	42 %	19 %
CdSe/19CdS-in water	187	42 %	27 %

Gdot blinking: work in progress and/or planned

- Duplicate analysis of new CdSe/*n*CdS batch
  - (before and after ligand exchange)
- Determination of bright and dark fractions in films
  - (≈ / ≥ Web et al. *PNAS* **2005**, *102*, 14284)
  - - using biotin(Gdot)-streptavidin(dye) conjugation
  - - correlation with ensemble QYs
- Effect(s) of annealing (Δ) & ligand loss (H.V.) on blinking

Acknowledgements

- Research supported by LANL LDRD and the DOE Center for Integrated Nanotechnologies

- Amy Casson