LA-UR- 08-5297

Approved for public release; distribution is unlimited.

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*
Intended for:	Oral presentation; 236th American Chemical Society National Meeting, Philadelphia, PA, Aug.16-21, 2008

Los Alamos
NATIONAL LABORATORY
EST.1943

Form 836 (7/06)

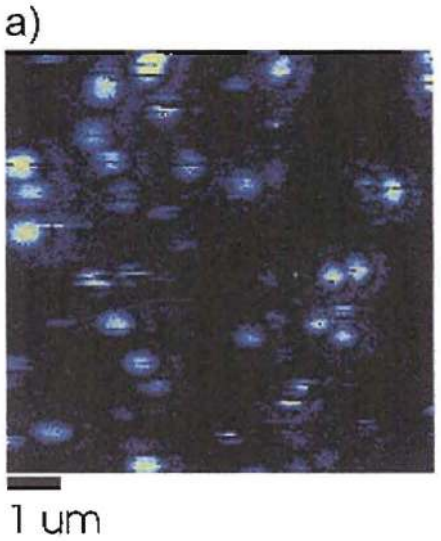
"Giant" Multishell CdSe Nanocrystal Quantum Dots With Suppressed Blinking

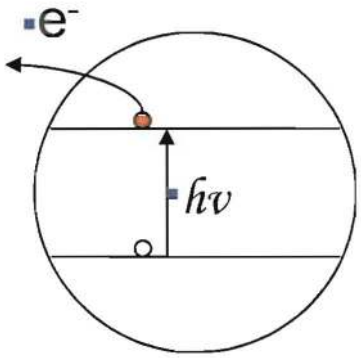
Yongfen Chen, **Javier Vela**, Han Htoon, Joanna L. Casson, Donald J. Werder, David A. Bussian, Victor I. Klimov, and Jennifer A. Hollingsworth*

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

236th ACS Fall National Meeting, Philadelphia, PA

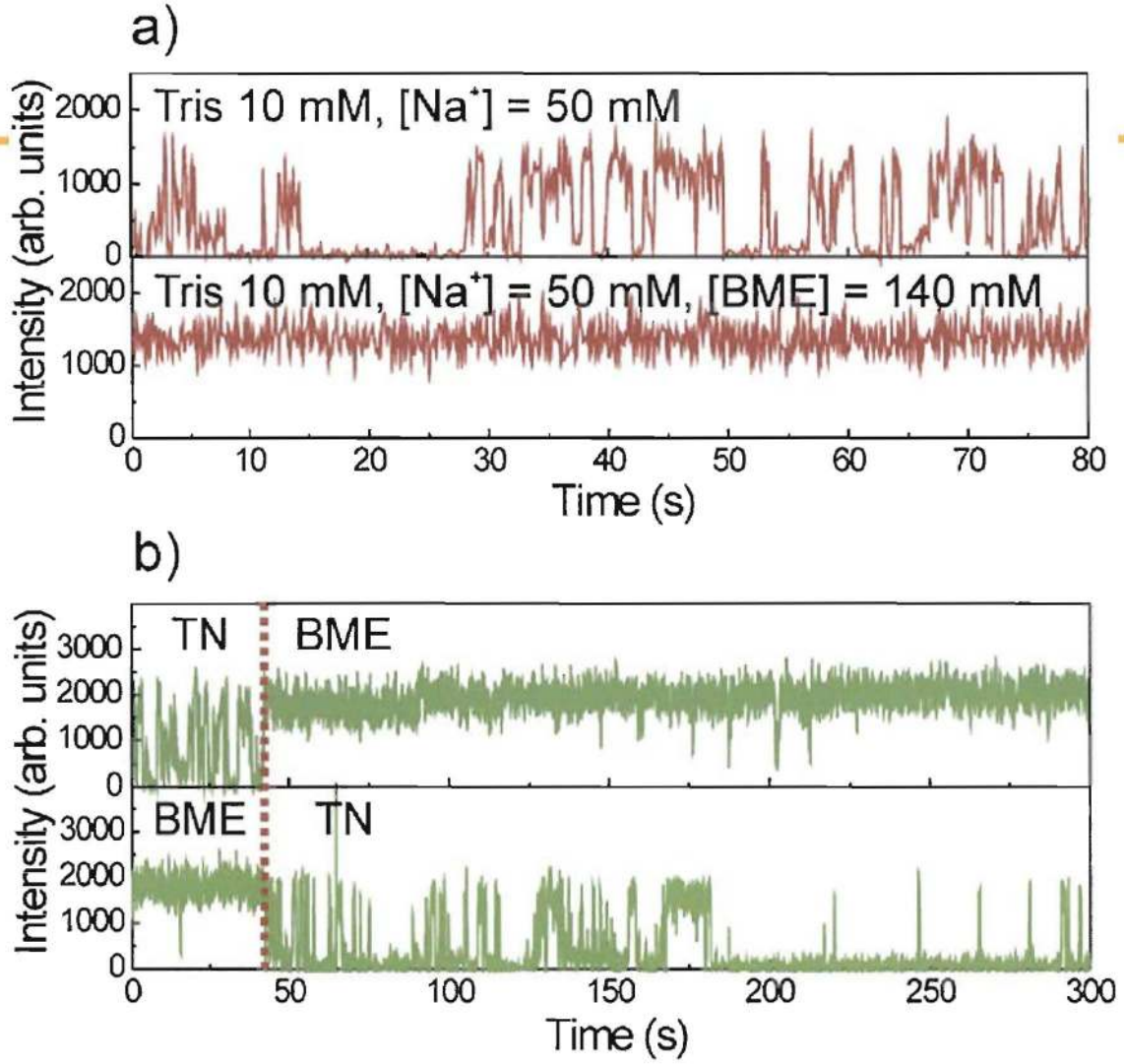
Fluorescence Intermittency of Single CdSe QDs





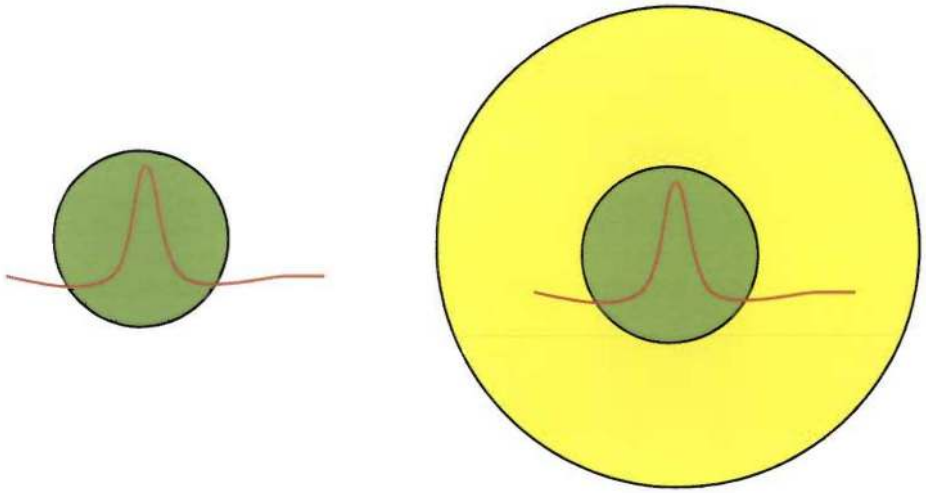
Nirmal, M.; B.O.Dabbousi, M. G. Bawendi, J.J. Macklin, J. K. Trautman, T. D. Harris, L. E. Brus. *Nature*. **1996**; 383.802-804.

- Way to suppress blinking

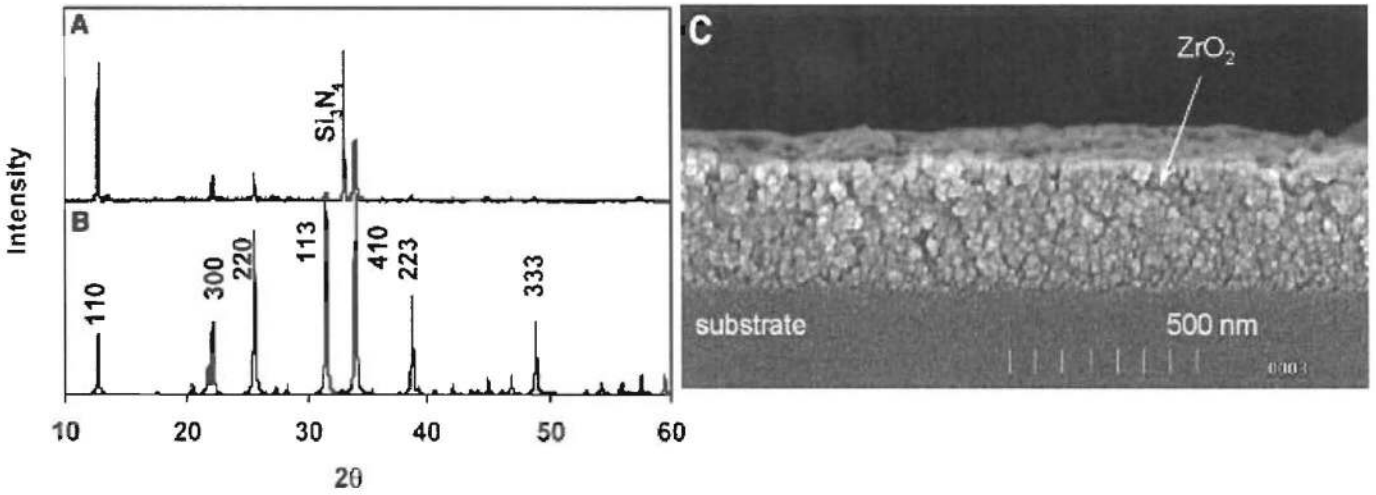


- Hohng, S.; Ha, T. *J. Am. Chem. Soc.*; **2004**; 126(5); 1324-1325

▪Complete confinement of wavefunction in a thick shell



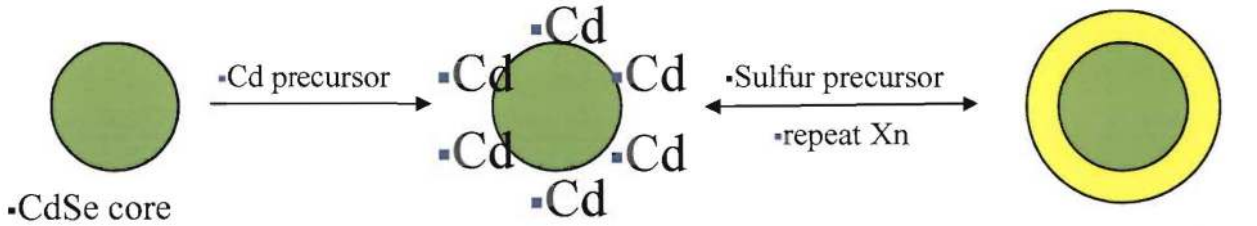
▪Original Succesive Ionic Layer Adsorption and Reaction (SILAR) for thin film prepration



▪(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.

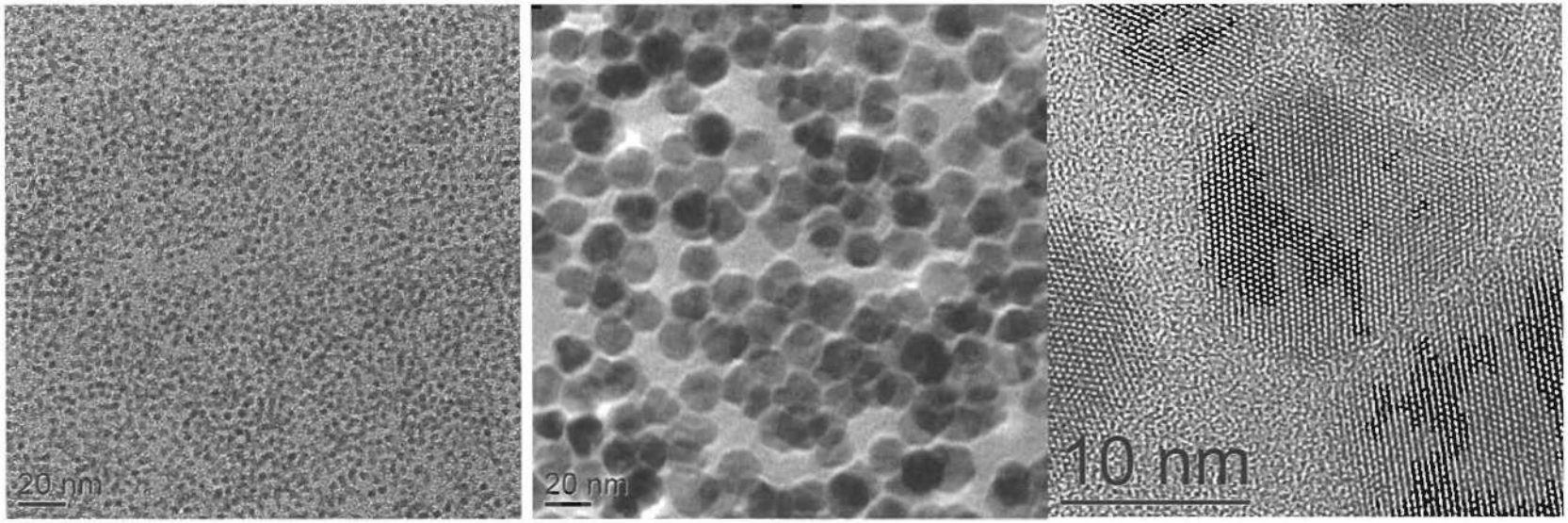
▪Sangmoon Park, Benjamin L. Clark, Douglas A. Keszler, Jeffrey P. Bender, John F. Wager, Thomas A. Reynolds, and Gregory S. Herman. **Low-Temperature Thin-Film Deposition and Crystallization** *Science* **2002** 297, 65

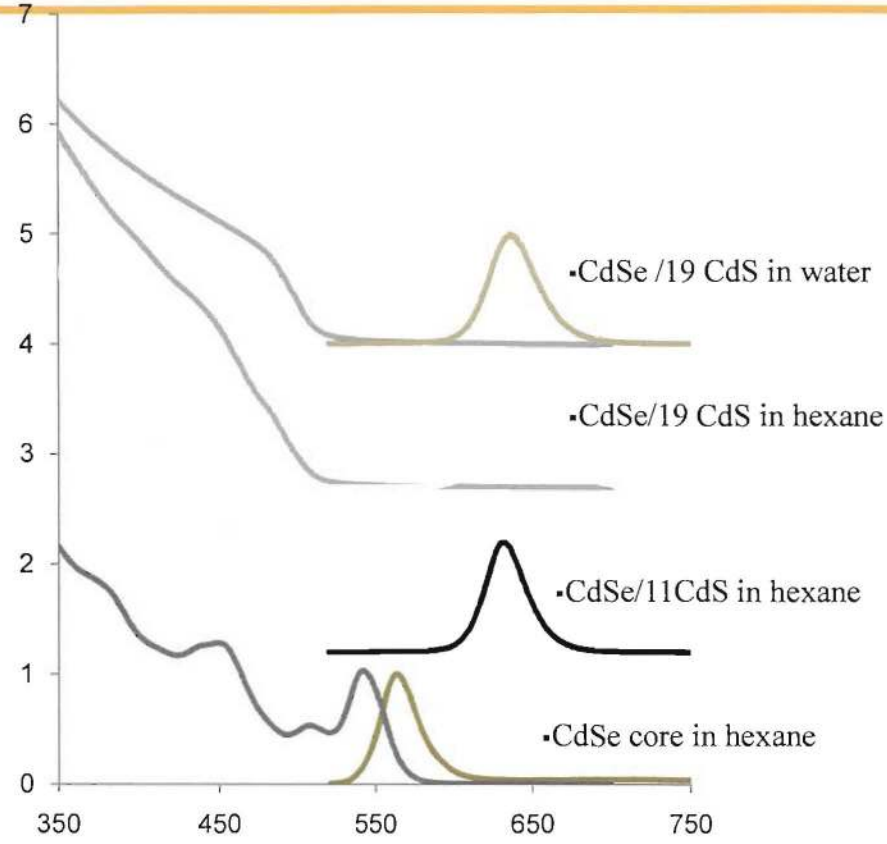
▪Modified SILAR method for Multishell CdS growth



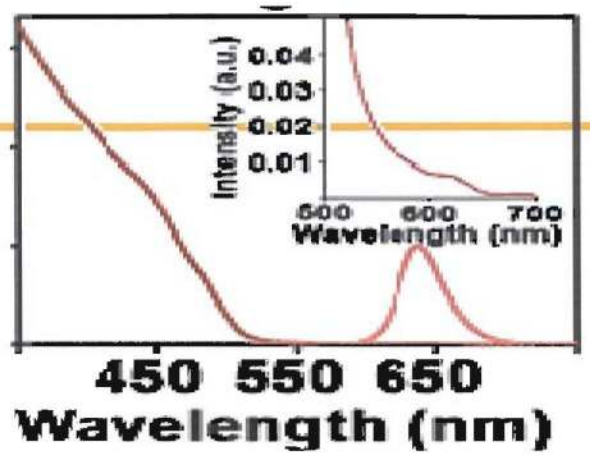
▪With Se rich surface

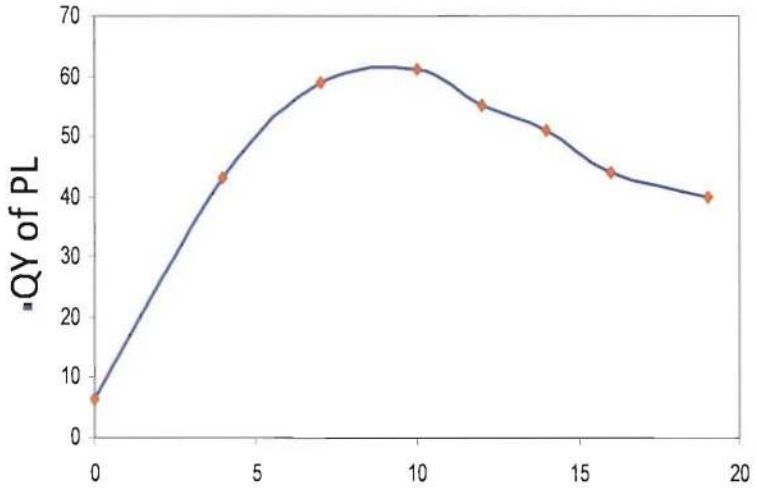
▪Li, J. J.; Wang, Y. A.; Guo, W.; Keay, J. C.; Mishima, T. D.; Johnson, M. B.; Peng, X. J. Am. Chem. Soc; **2003**; 125(41); 12567-12575


20 nm
20 nm
10 nm



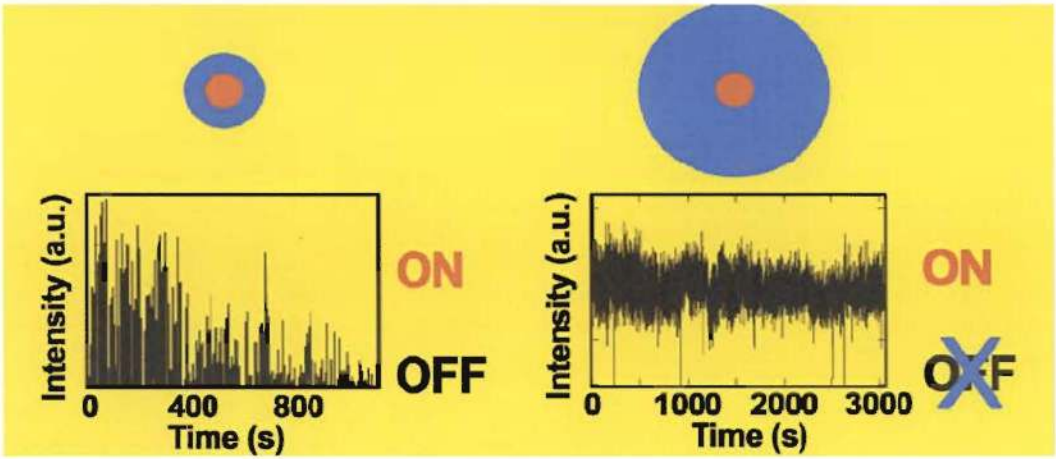
▪Wave length (nm)





▪Number of CdS monolayer

"Giant" Multishell CdSe Nanocrystal Quantum Dots With Suppressed Blinking

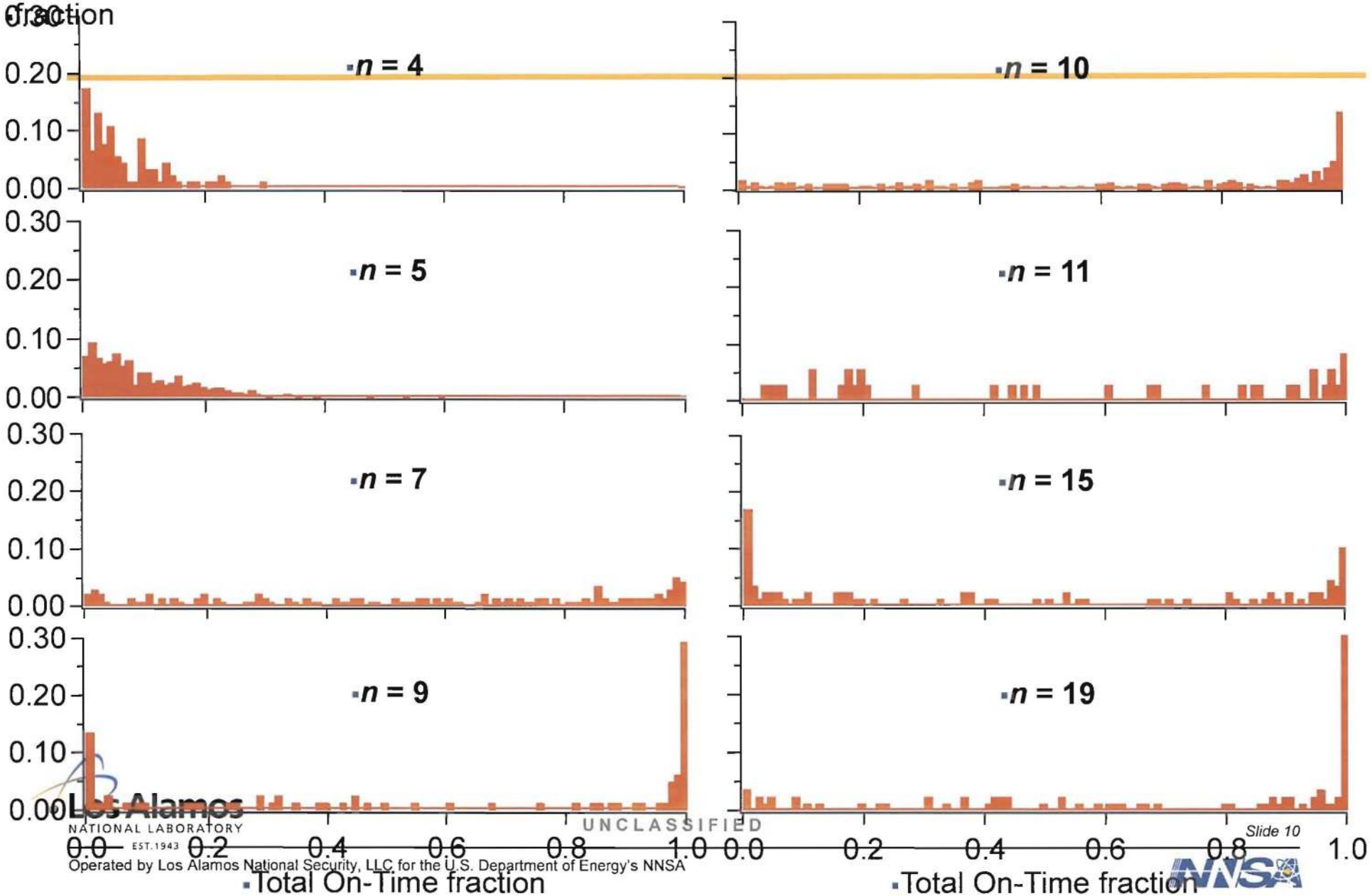


- Chen et al. *JACS* **2008**, *130*, 5026

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

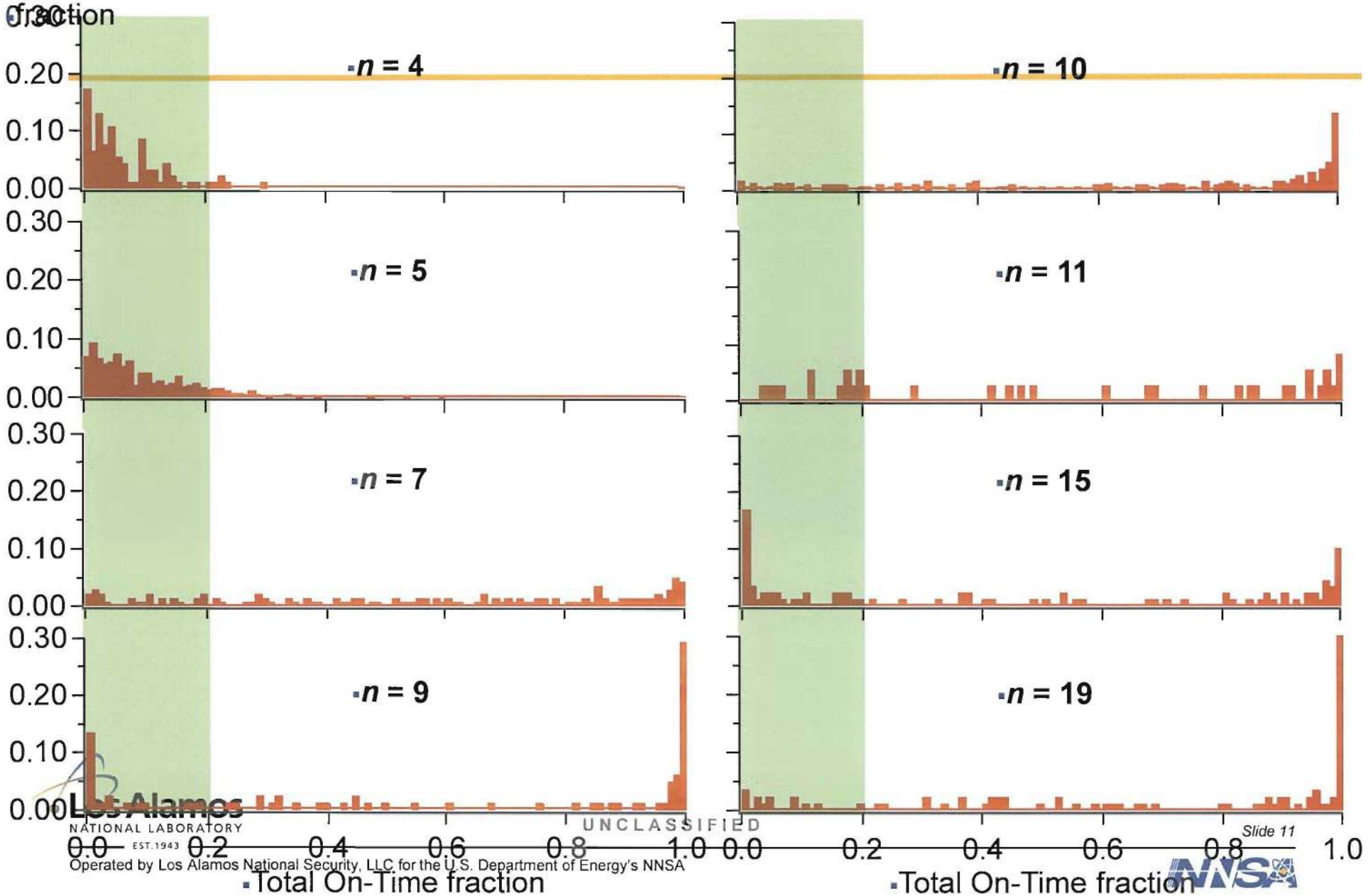
▪CdSe/*n*CdS: Blinking behavior over time

▪NQD

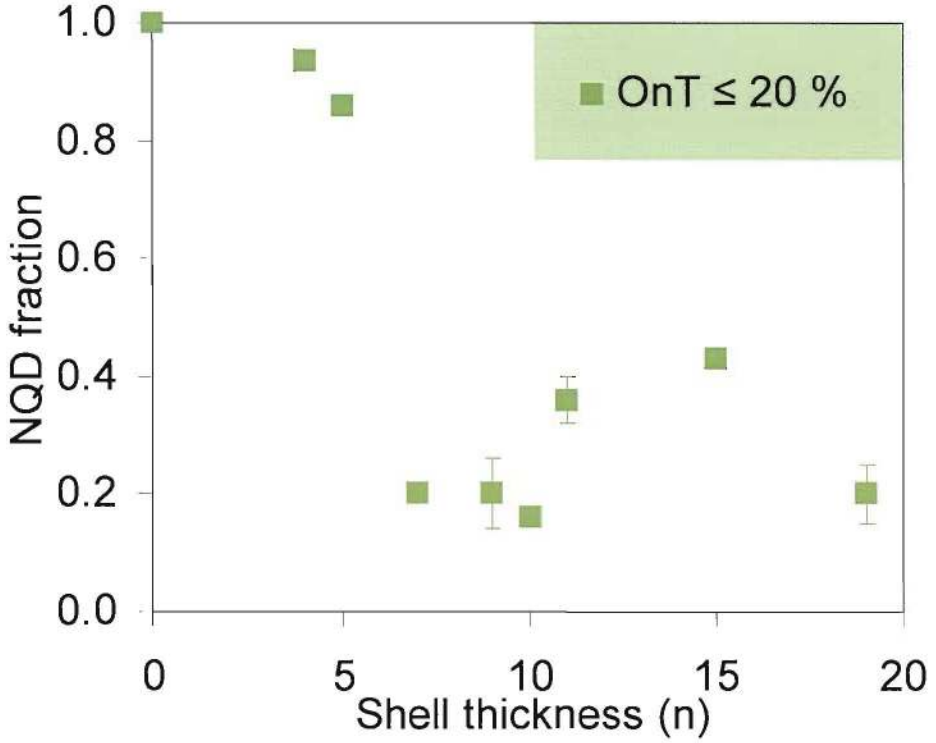


▪CdSe/*n*CdS: Blinking behavior over time

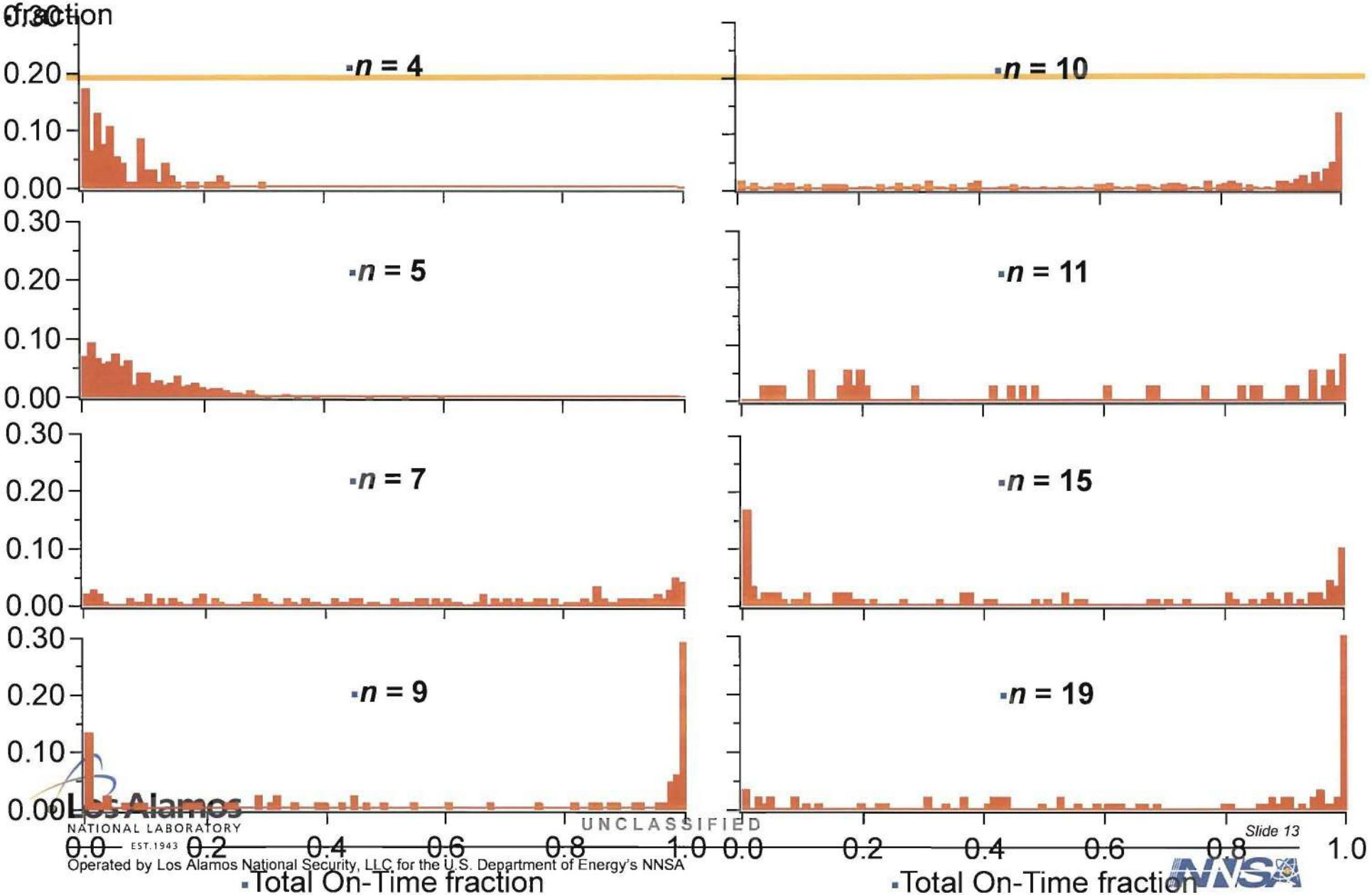
▪NQD



Blinking behavior vs. shell thickness (n)

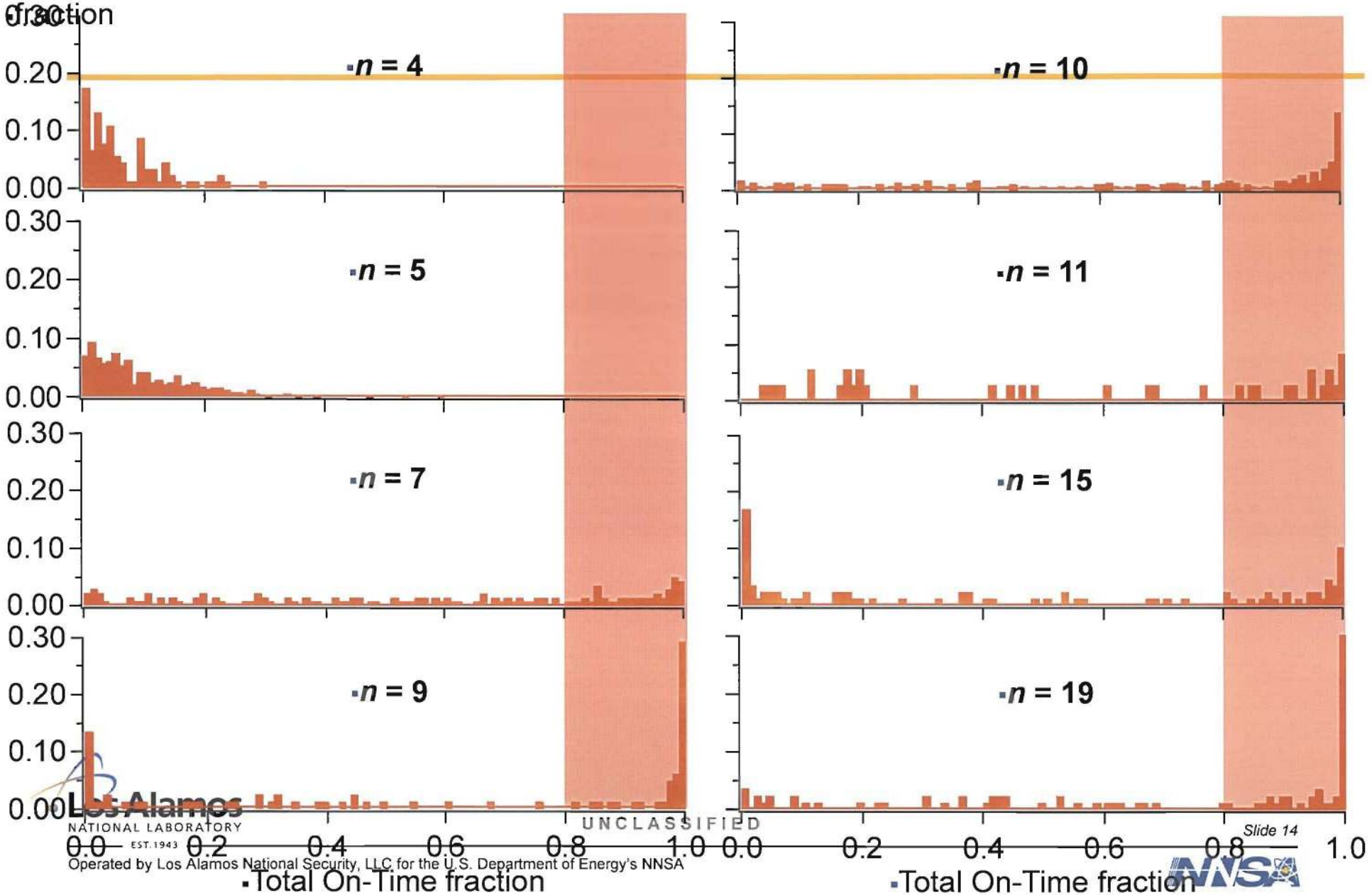


▪CdSe/*n*CdS: Blinking behavior over time

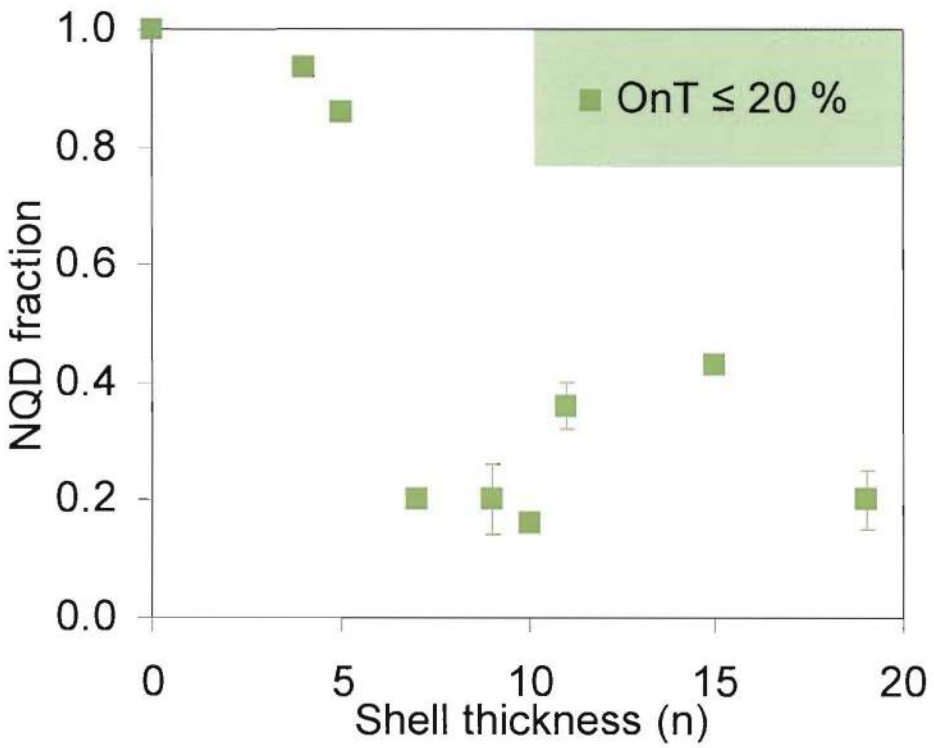


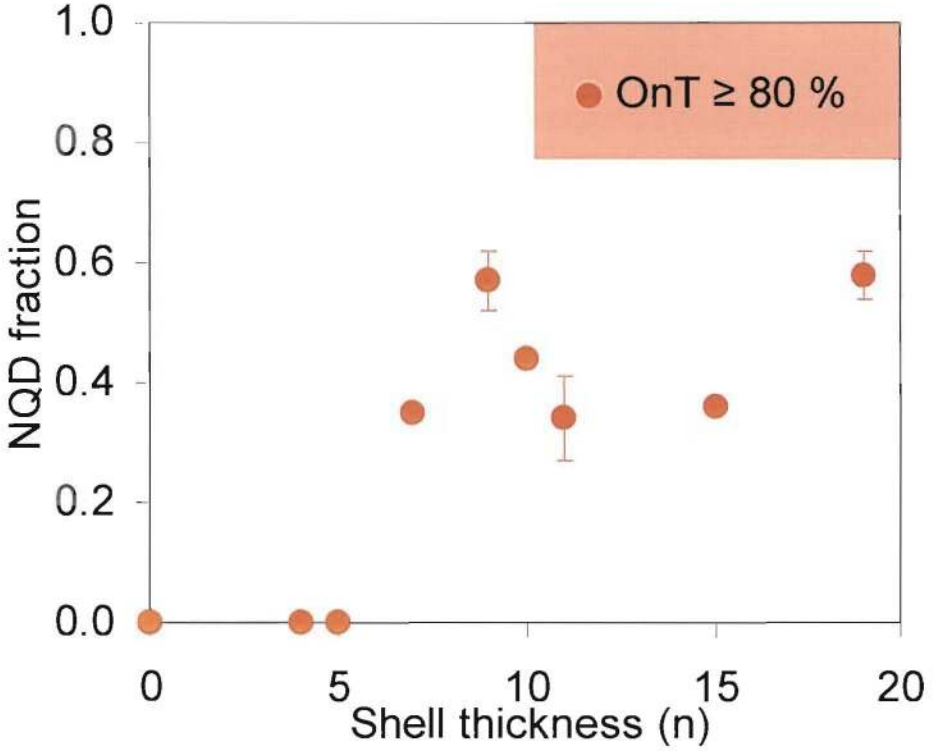
▪CdSe/*n*CdS: Blinking behavior over time

▪NQD



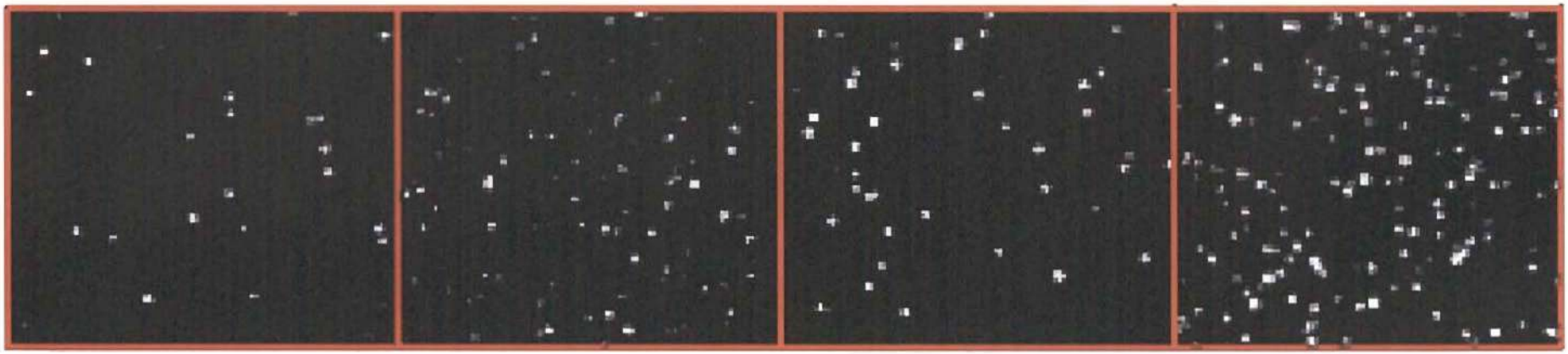
Blinking behavior vs. shell thickness (n)



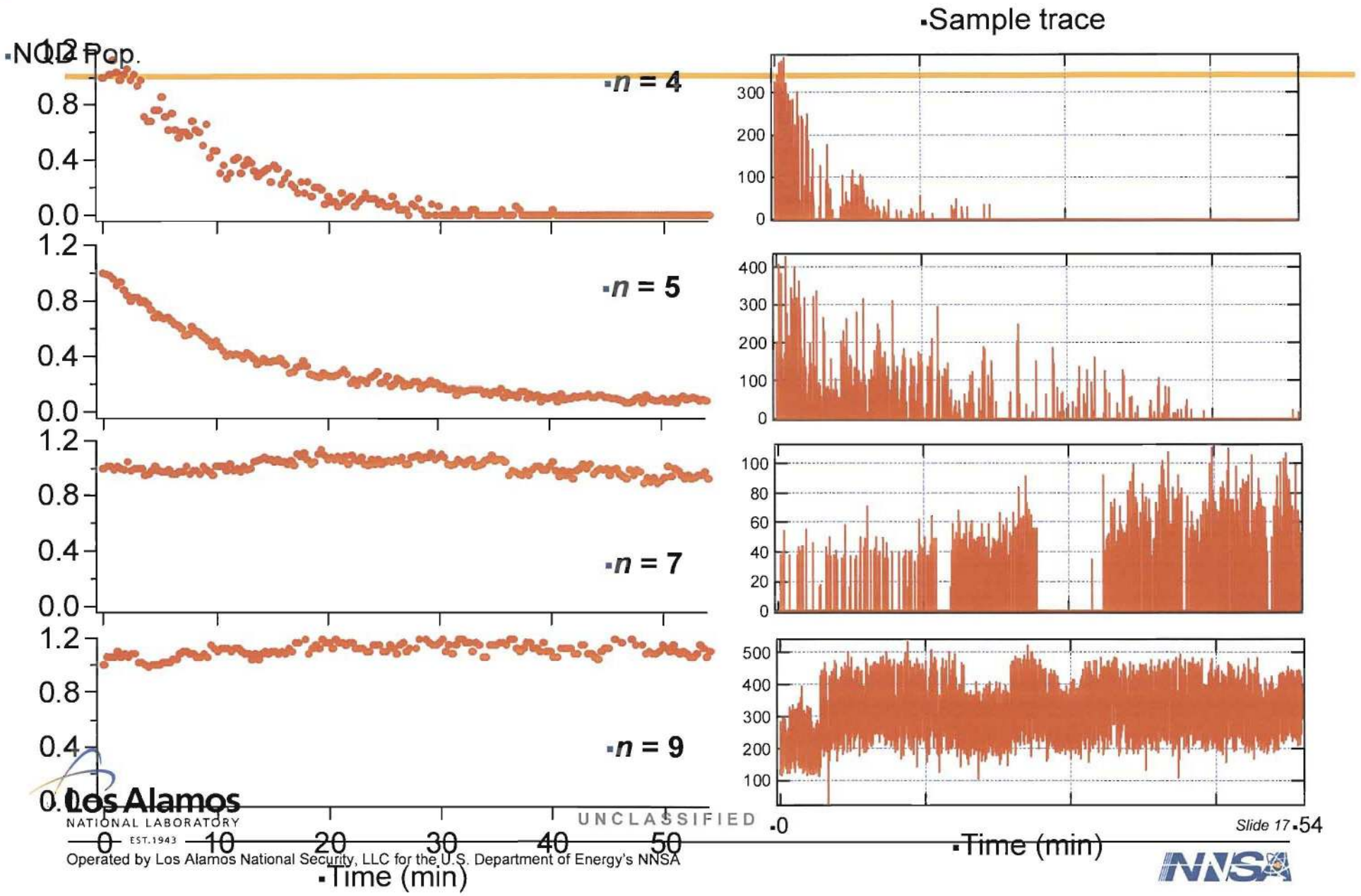


Gdot blinking: How does it look like?

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



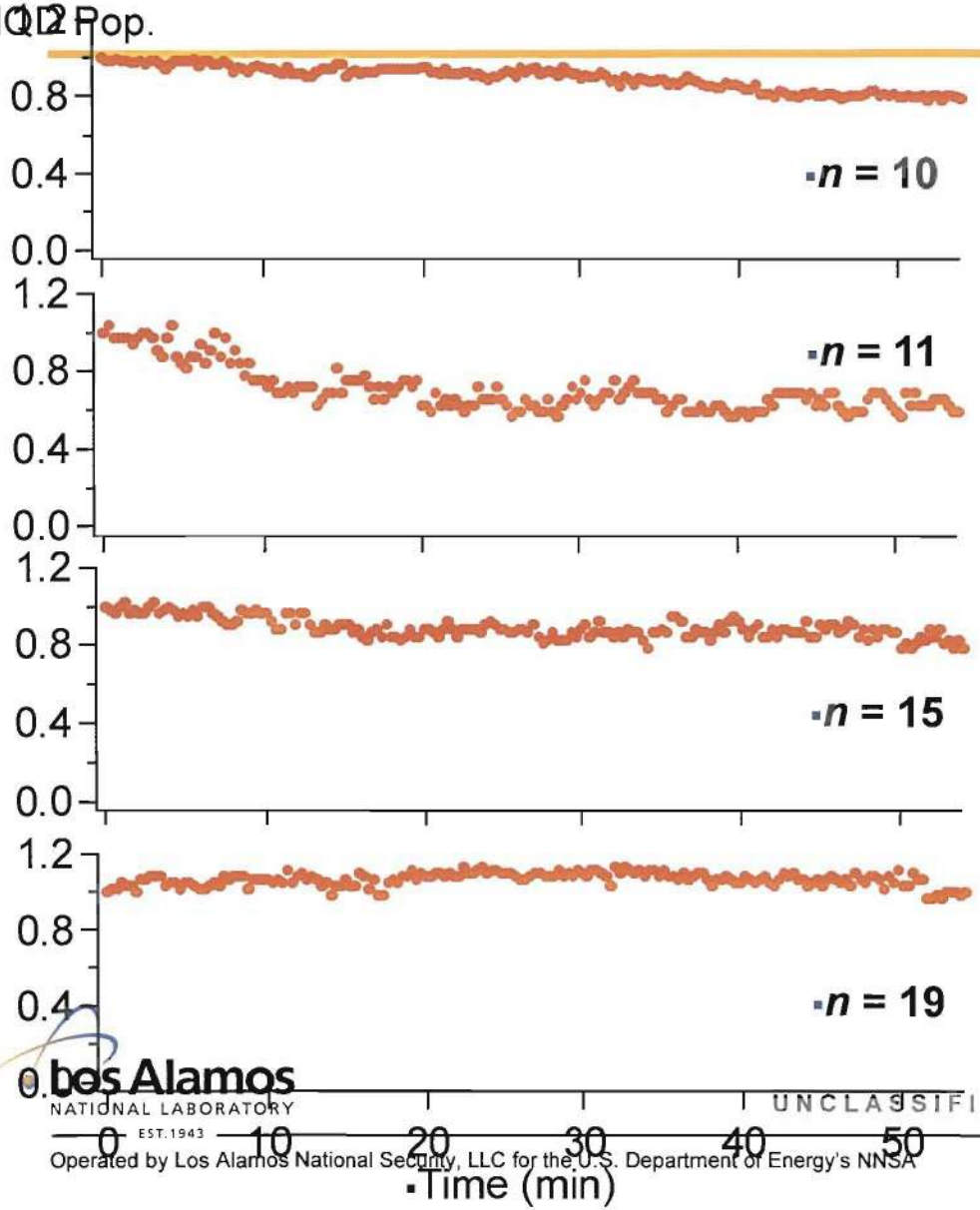
▪CdSe/*n*CdS: Photostability



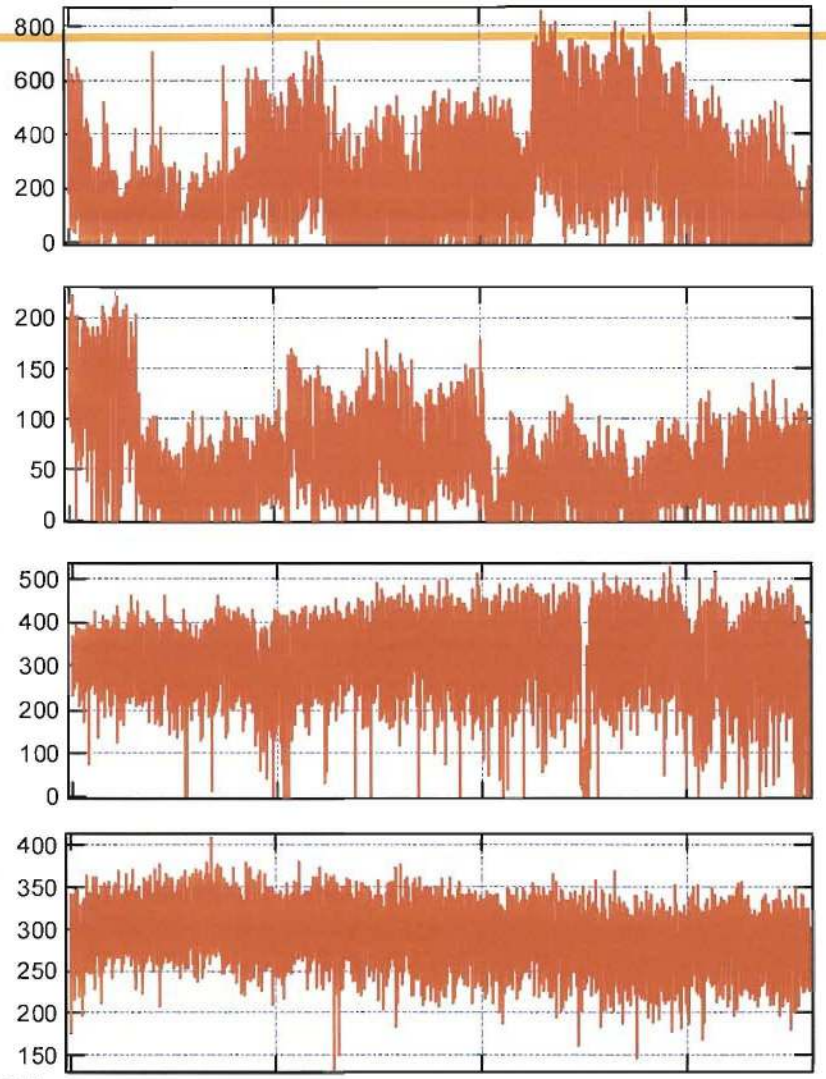
▪CdSe/*n*CdS: Photostability

▪Normalized

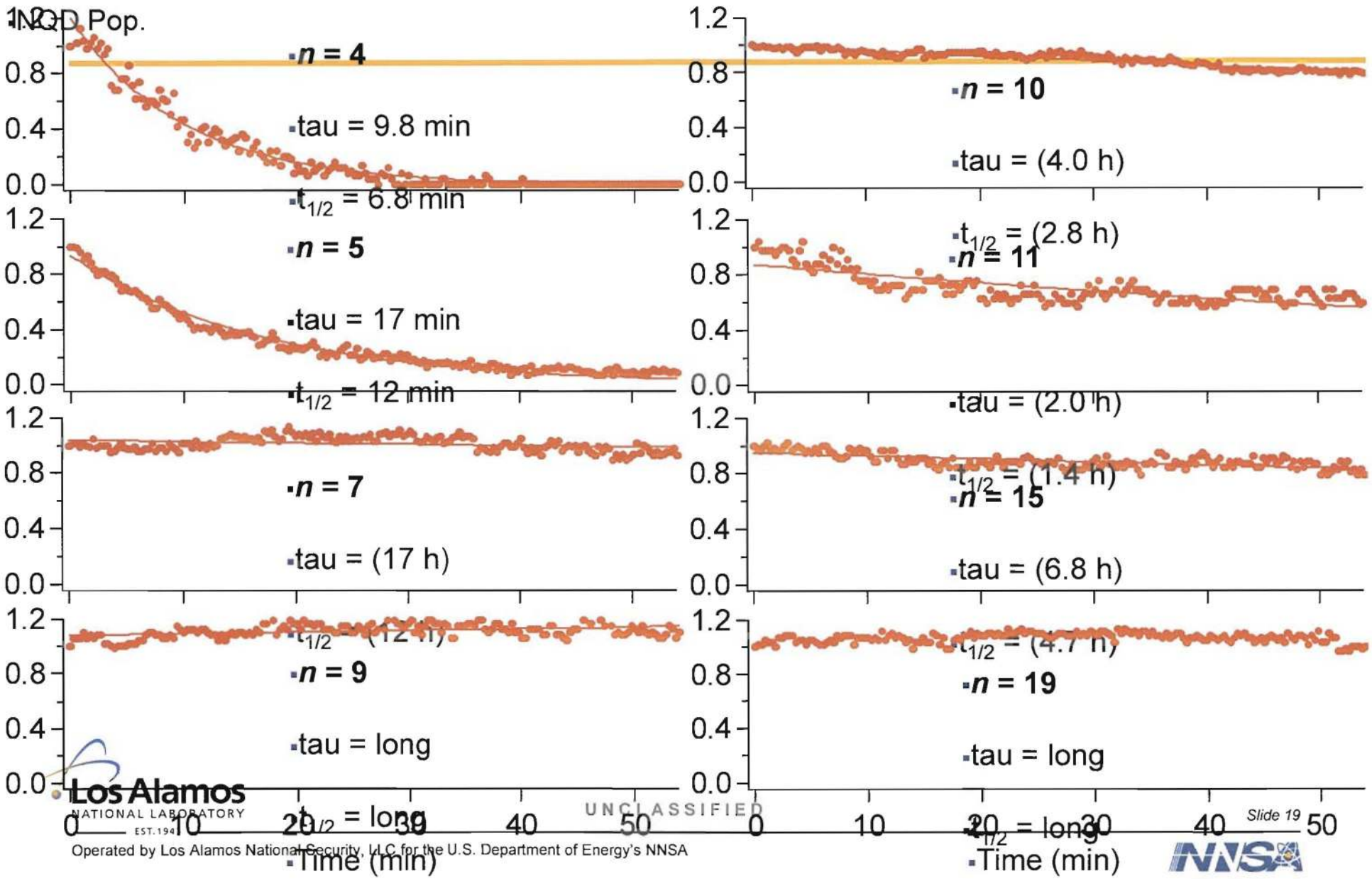
▪NQD Pop.



▪Sample trace

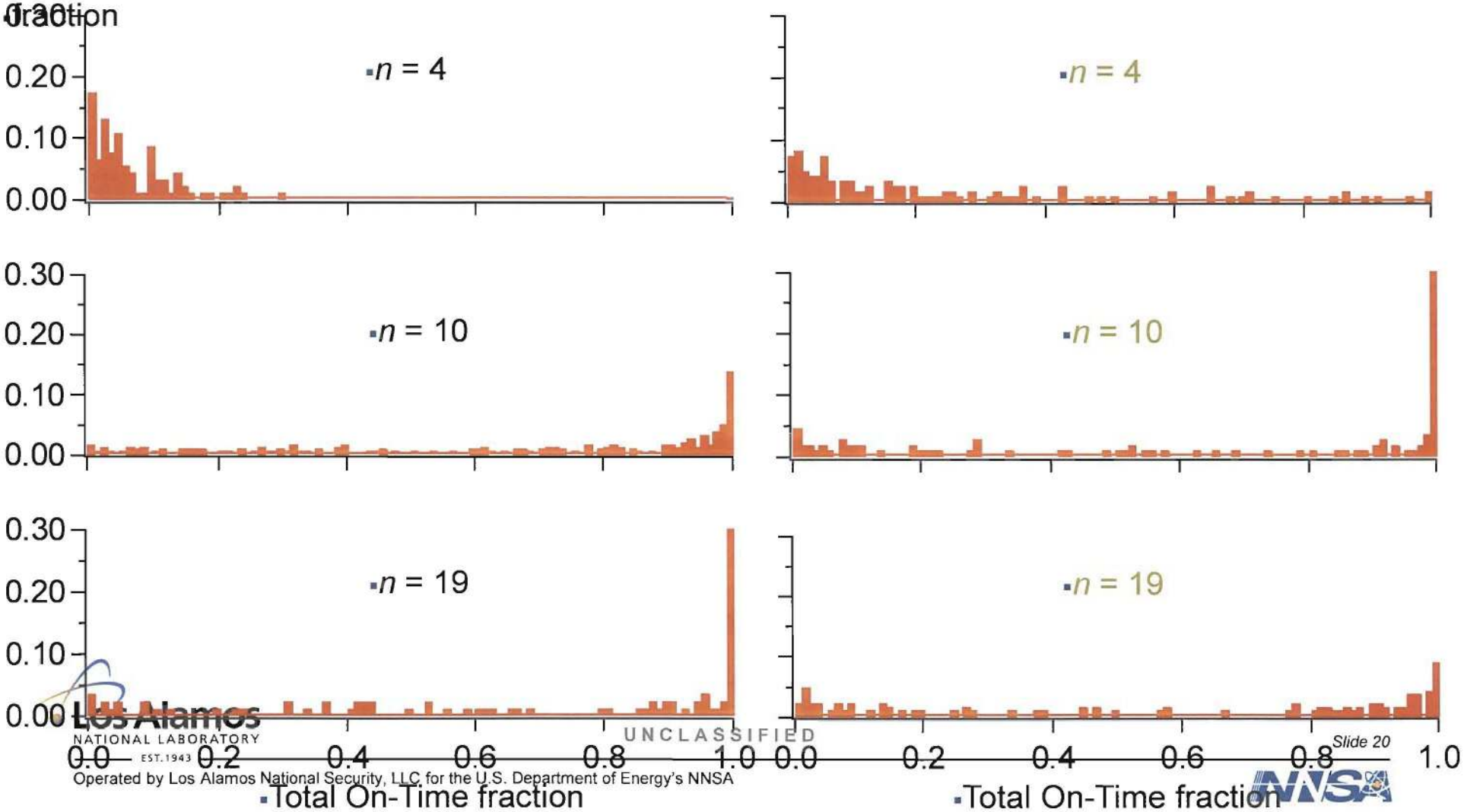


CdSe/*n*CdS: Photostability



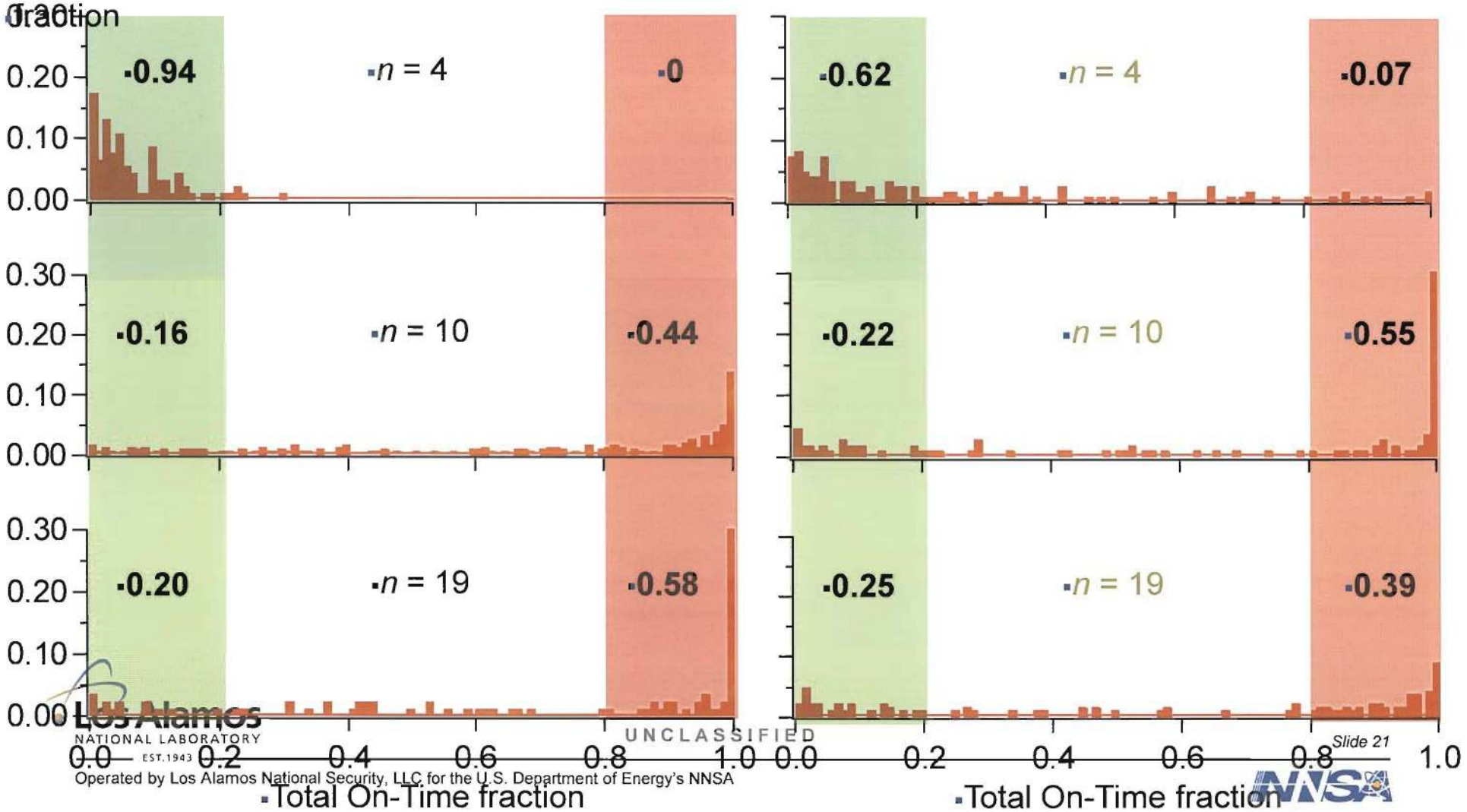
CdSe/*n*CdS: Blinking behavior vs. ligand & solvent

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



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



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.

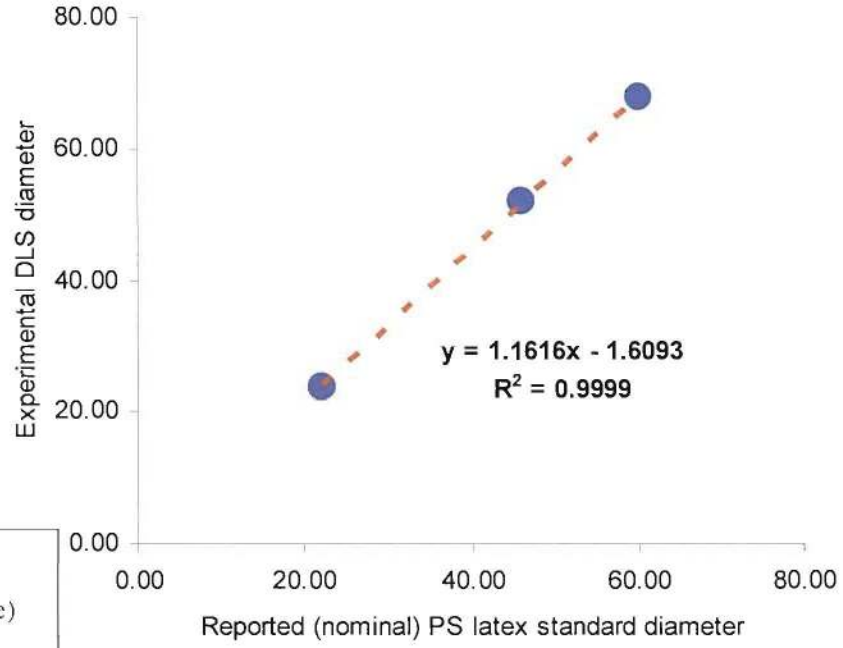


Table S2. Comparison of TEM-derived total size with DLS-derived total size.

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