Quantum Dot (QD) Down-converters: Quantum Yield, Stability, Scale-up

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QD materials optimization & validation for SSL – DOE EERE

Office of Basic Energy Sciences – Serving the Present, Shaping the Future

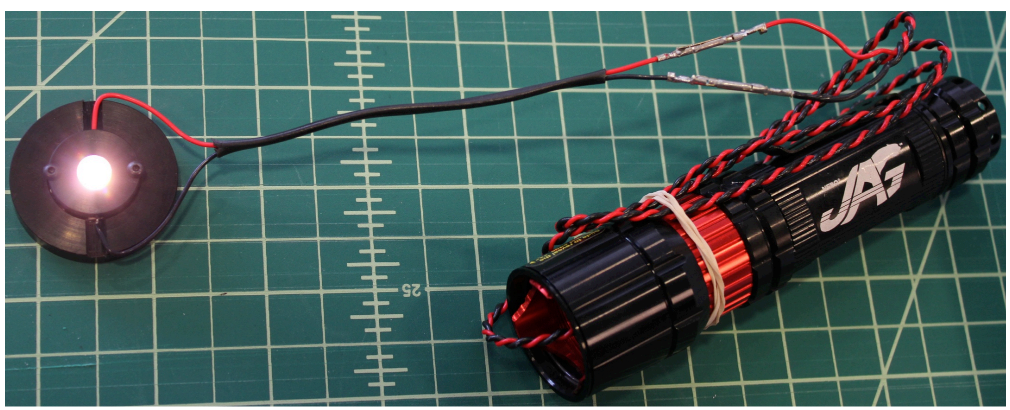
U.S. DEPARTMENT OF ENERGY – Energy Efficiency & Renewable Energy

Applied R&D needs for <u>on-chip</u> QD phosphors:

- High QY (>90%)
- Minimal/no thermal quenching
- Reliability under conditions of elevated temperature (to 115 ºC), photon flux (1-5 W•mm^{-2}) and humidity (to 85%)

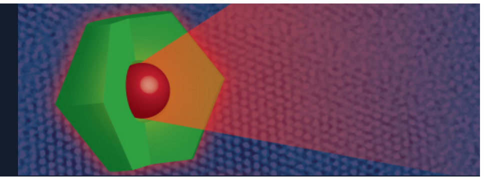
<u>Opportunity</u>: Take advantage of QD traits that enable a large color gamut and improved color quality for efficiency gains

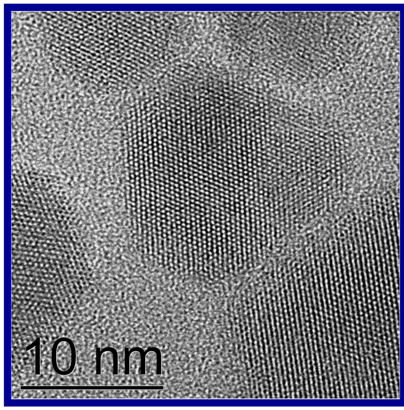
<u>Key technical challenge</u>: High QY paired with lifetime reliability under high flux and high temperature

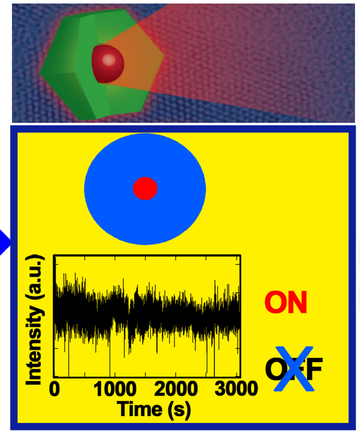


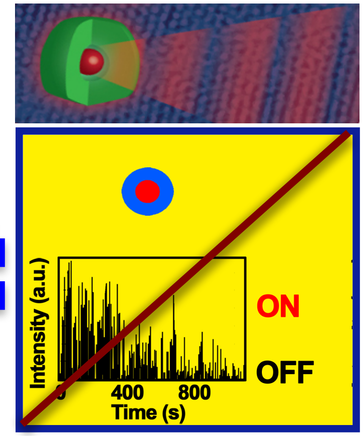
Our demo warm-white "giant"-QD LED

Long history in creating stable QDs







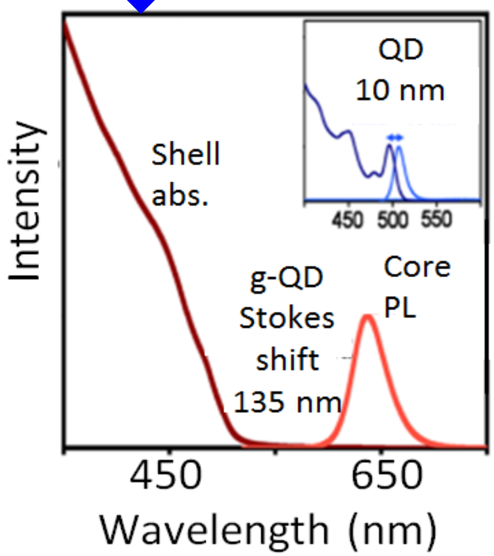


I. Superior photo-stability at single-emitter level

A. *Non-blinking*

B. *Non-bleaching*

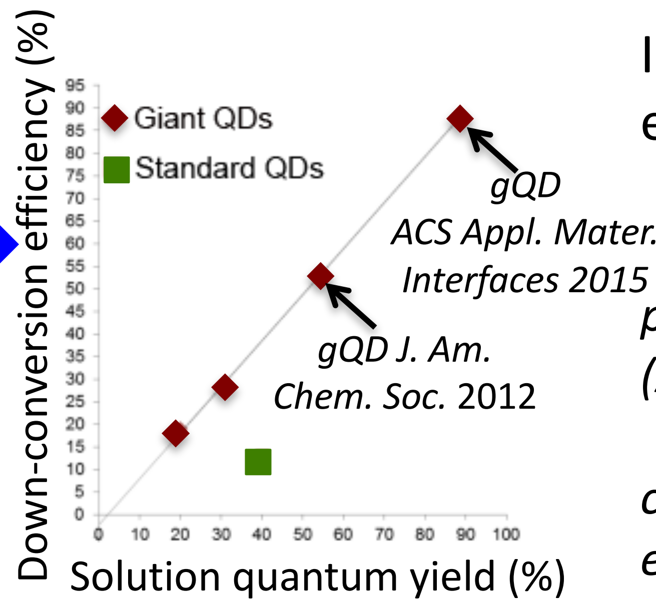
gQD J. Am. Chem. Soc. 2008



II. Non self-reabsorbing

A. *Large "Stokes shift"*

gQD J. Am. Chem. Soc. 2008



III. Solid-state efficiency

A. *Non self-absorbing*

B. *Non-radiative processes suppressed (Auger, energy-transfer)*

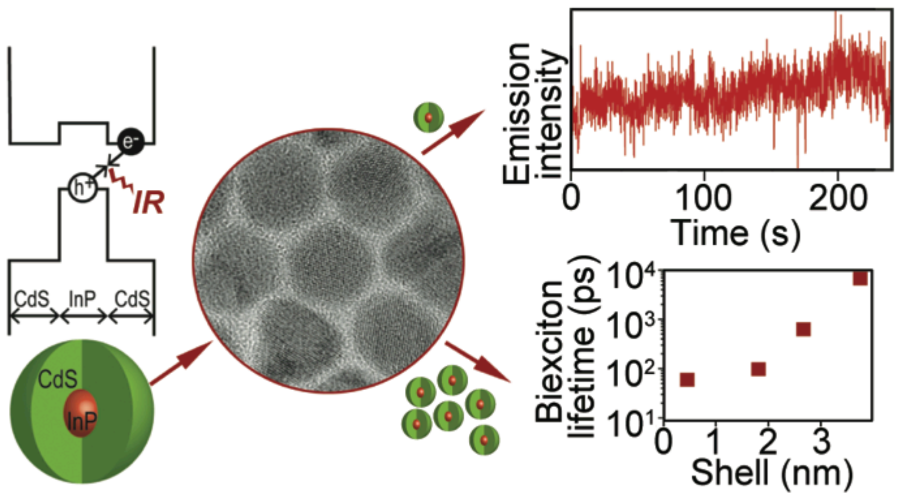
C. *Large absorption cross-section ("antenna effect")*

- Patented novel functionality: *Thick-shell "Giant" Quantum Dots (gQDs) US Patent 7,935,419*

Does approach apply to other QDs?

- Yes, and shell thickness and electronic structure seem to be overriding parameters

InP/CdS Type II thick-shell QDs –
Blinking-suppressed infrared emission



Dennis et al. *Nano Lett.* 2012

CdSe/CdS size & shape-tuned tetrapods –
2-color blinking suppression

Image removed

PbSe/CdSe Quasi Type II thick-shell QDs –
Blinking/extreme bleaching-suppressed infrared emission

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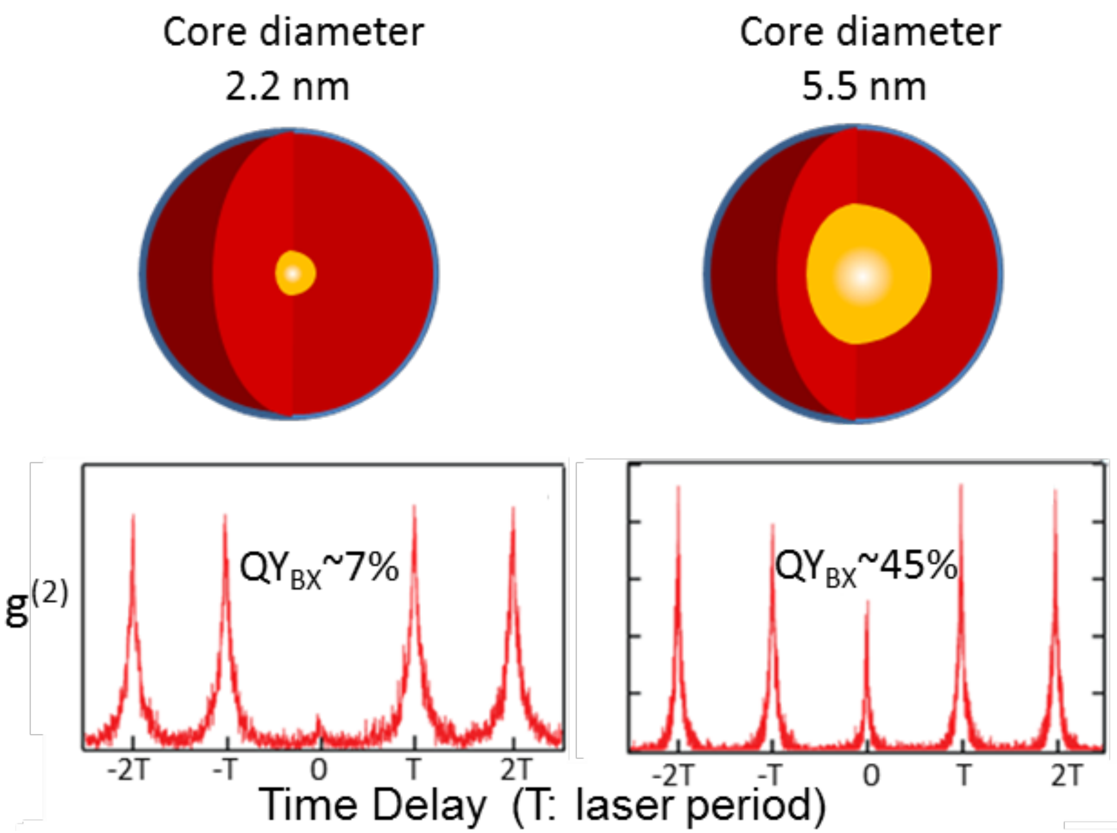
Unexpected effect of core size

- Same total particle volume, different core size → different Auger suppression

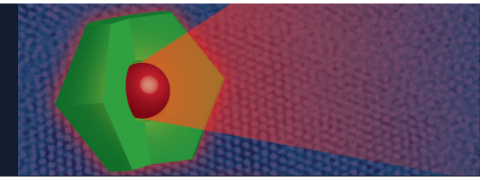
Revisiting CdSe/CdS…



And, *large core + thick shell*: Biexciton (BX) QYs approach 100%

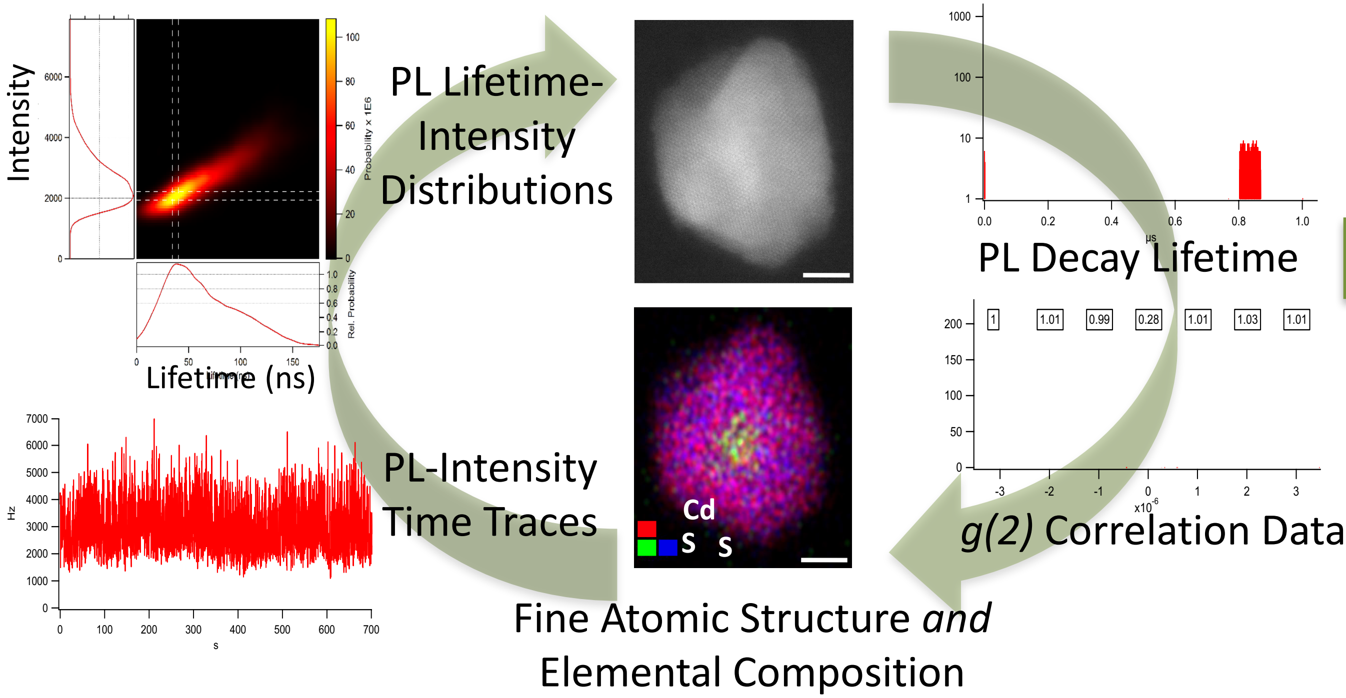
Mangum et al. *Nanoscale* 2014

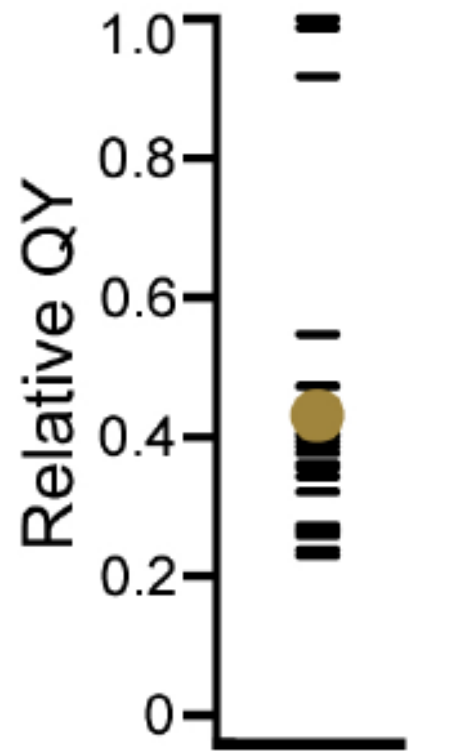
gQDs for SSL?



Challenge: Efficiency

- Why do non-blinking gQDs have <100% QY?
  - * *New technique*: Correlated optical/structural characterization
  - * *New understanding*: Orfield et al. *ACS Nano* 2016
    - \- No dark gQDs
    - \- QYs by "pinning" to charge states
    - \- <u>No fundamental limit to gQD QYs</u>



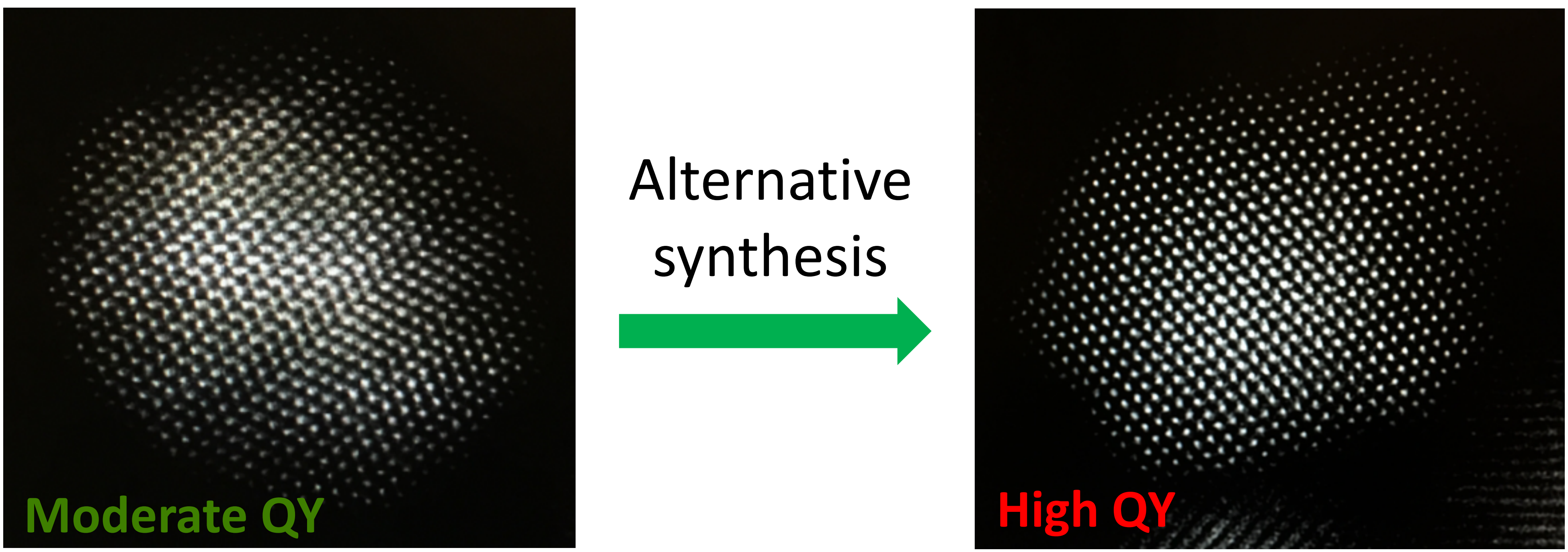


(Mean QY = 43%)

gQDs for SSL?

Challenge: Efficiency

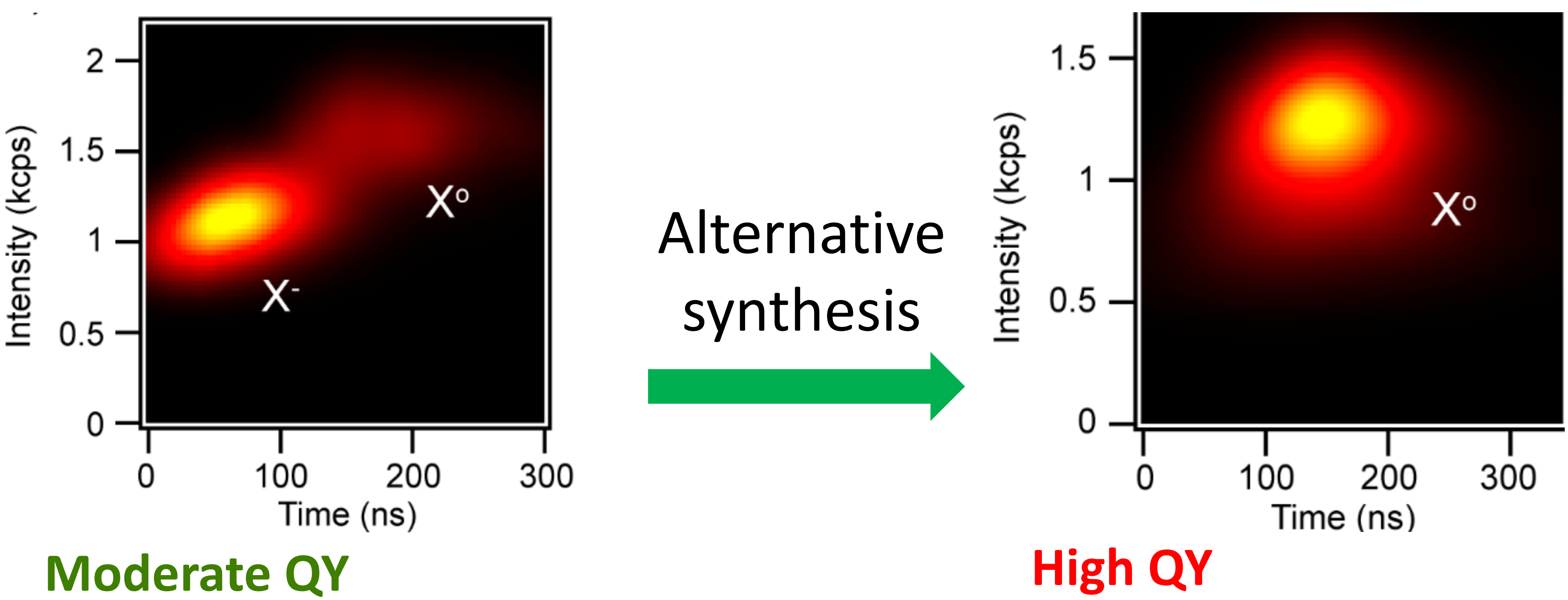
- Challenge addressed through changes to synthesis ➔ 75-90% QYs
    - * *Advanced characterization*: Imaging, compositional analyses reveal synthesis-dependent internal structure
    - * *New result*:
        - - Ultra-bright gQDs have more perfect internal structure



gQDs for SSL?

Challenge: Efficiency

- Why are new gQDs brighter?
  - ** Emit from neutral exciton state*
  - ** Moderate-QY gQDs emit from neutral and charged states*

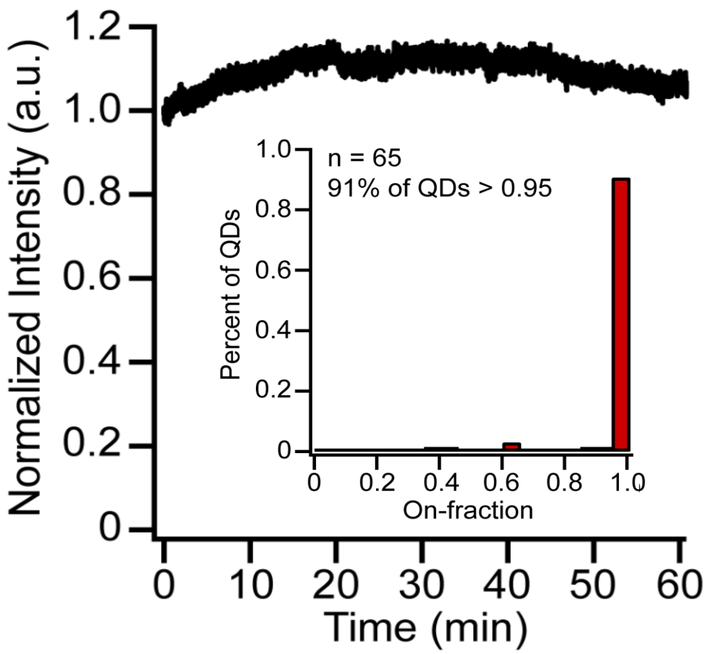


gQDs for SSL?

Challenge: Stability

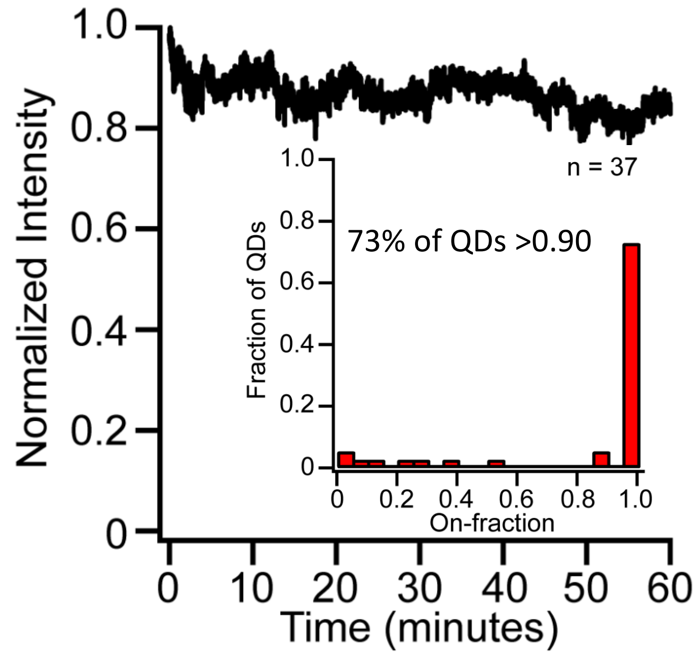
- Our initial criterion: Room-T single-dot bleaching and blinking

  * *Moderate and high-QY gQDs exhibit similar behavior*



Moderate QY

Alternative synthesis



High QY

Lifetime tests

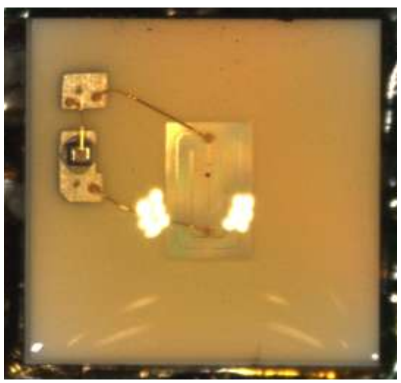
HTOL device testing

- Temperature and flux

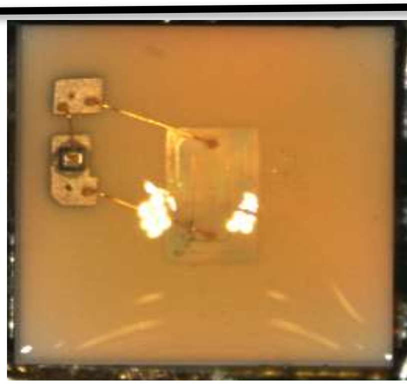
  * Device performance is chemistry/structure dependent

    (a) Mod-QY gQD maintains QY after curing in silicone and after >300 h HTOL lifetime testing (85 ^{0}C, 175 mA)

    (b) Hi-QY gQD does not



Mod-QY gQD	0 h Cured QY (T_0)	168 h QY (T/T_0)	336 h QY (T/T_0)
Soln QY (40%)	36% (1.0)	41% (1.14)	37% (1.03)



Hi-QY gQD	0 h Cured QY (T_0)	168 h QY (T/T_0)	336 h QY (T/T_0)
Soln QY (85%)	57% (1.0)	NA	34% (0.60)

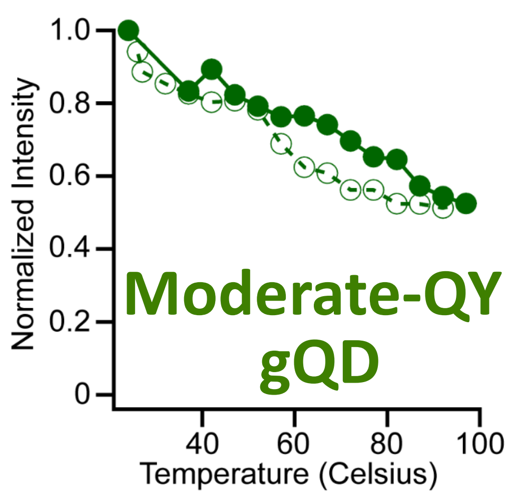
Lifetime tests

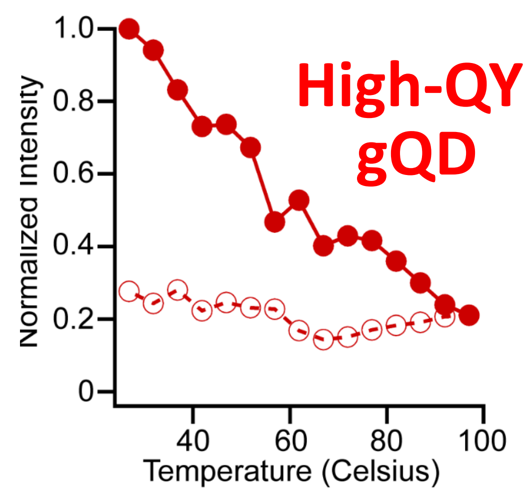
Single-dot stress tests

- Temperature and flux
  - * Emission recovery after combined temperature and flux stressors is chemistry/structure dependent
    - (a) Mod-QY gQD PL recovers; most brighten!
    - (b) Hi-QY gQD PL does not recover; many 100% bleached

Out-and-back recovery comparison

- High flux = 15 W•mm^{-2}
- ***Moderate-QY (50%) gQD***
- ***High-QY (80%) gQD***





Lifetime test

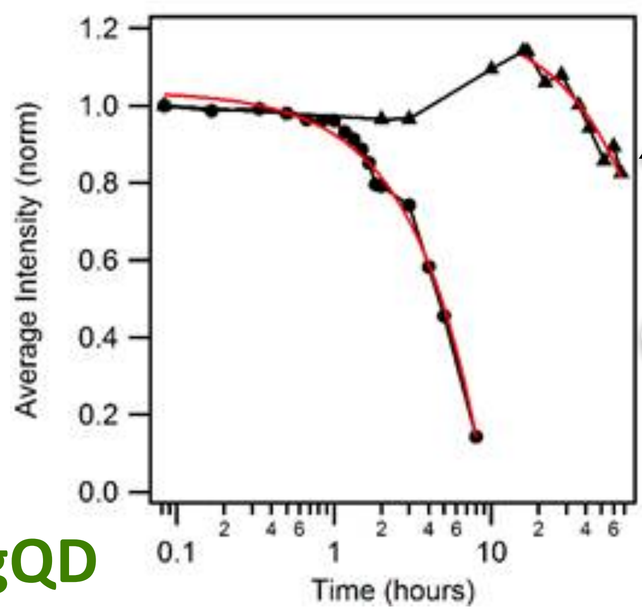
Single-dot stress tests

- Temperature and flux

(a) Mod-QY gQDs withstand flux and heat; no gQD is completely bleached

(b) Hi-QY gQDs permanently photobleach after brief exposure to flux (1 or 10 W/mm^2) and heat (100 ^{0}C)

<u>Single-dot heat/flux stress tests: *Long-term thermal exposure*</u>



▲ 0.1 W/mm^2, 100 ^{0}C

● 10 W/mm^2, 100 ^{0}C

Moderate-QY gQD

Two photobleaching mechanisms

Different processes lead to lifetime instability

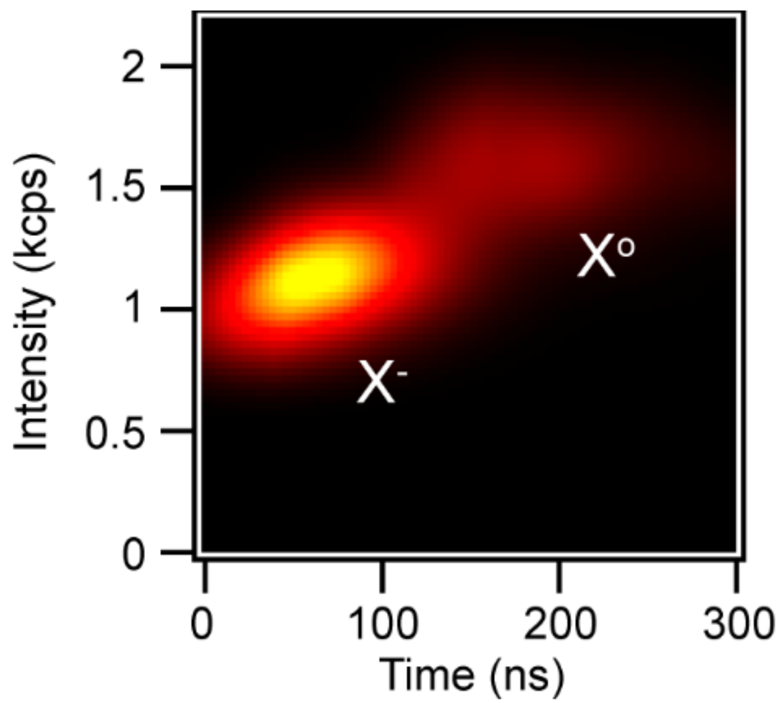
- Mod-QY gQDs → "A-Type"

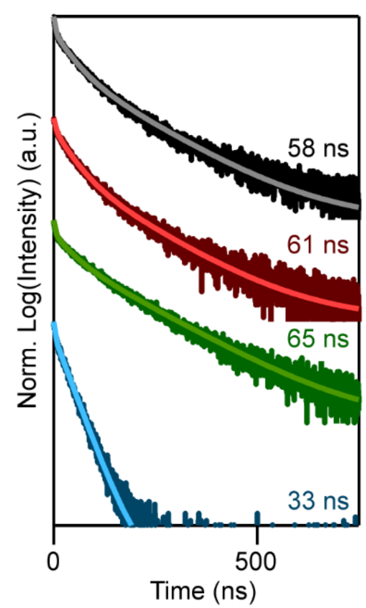
  (a) Bleaching through increased dot charging

  (b) Never completely bleach,

  but neutral (brighter) exciton ceases

  to contribute to PL over time

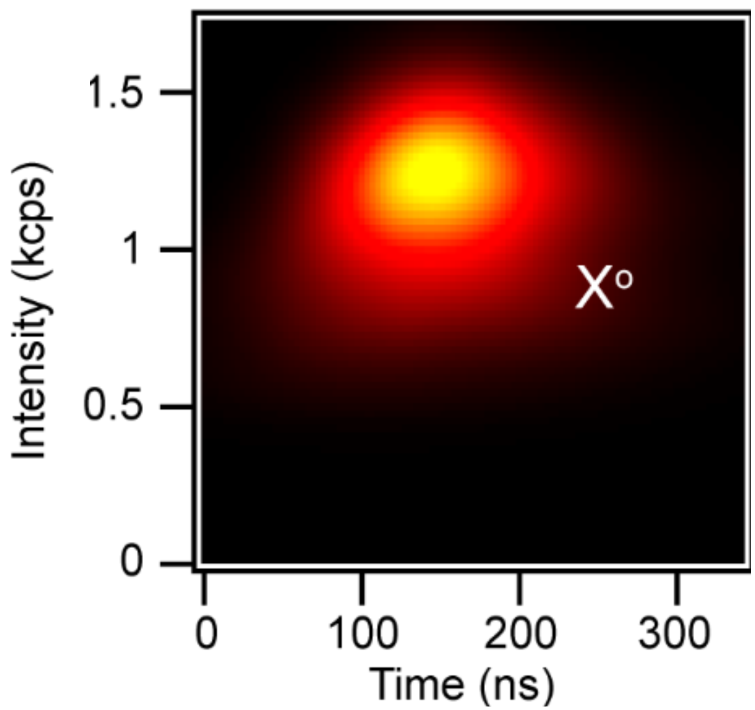


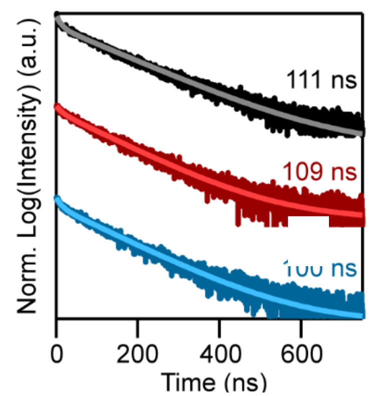


Two photobleaching mechanisms

Different processes lead to lifetime instability

- Hi-QY gQDs → "B-Type"
  - (a) Bleaching through increased surface trapping
  - (b) Neutral exciton dominates PL, but then fails catastrophically





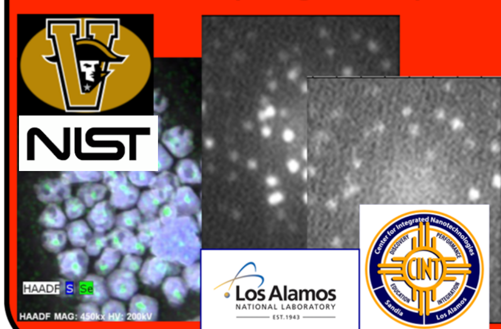
Progress toward practical gQD performance via closed-loop approach

Synthesis in an automated reactor system & *in situ* diagnostics

Microscopy feedback: Establish dot-to-dot uniformity & 100% optimal structures

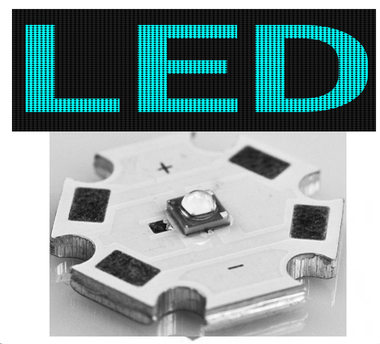
Synthesis feedback: Establish high efficiency, 'drop-in' performance & lifetime robustness

Correlated structure-optical studies (single-dot)



Performance feedback: Establish structure-function correlated failure mechanisms

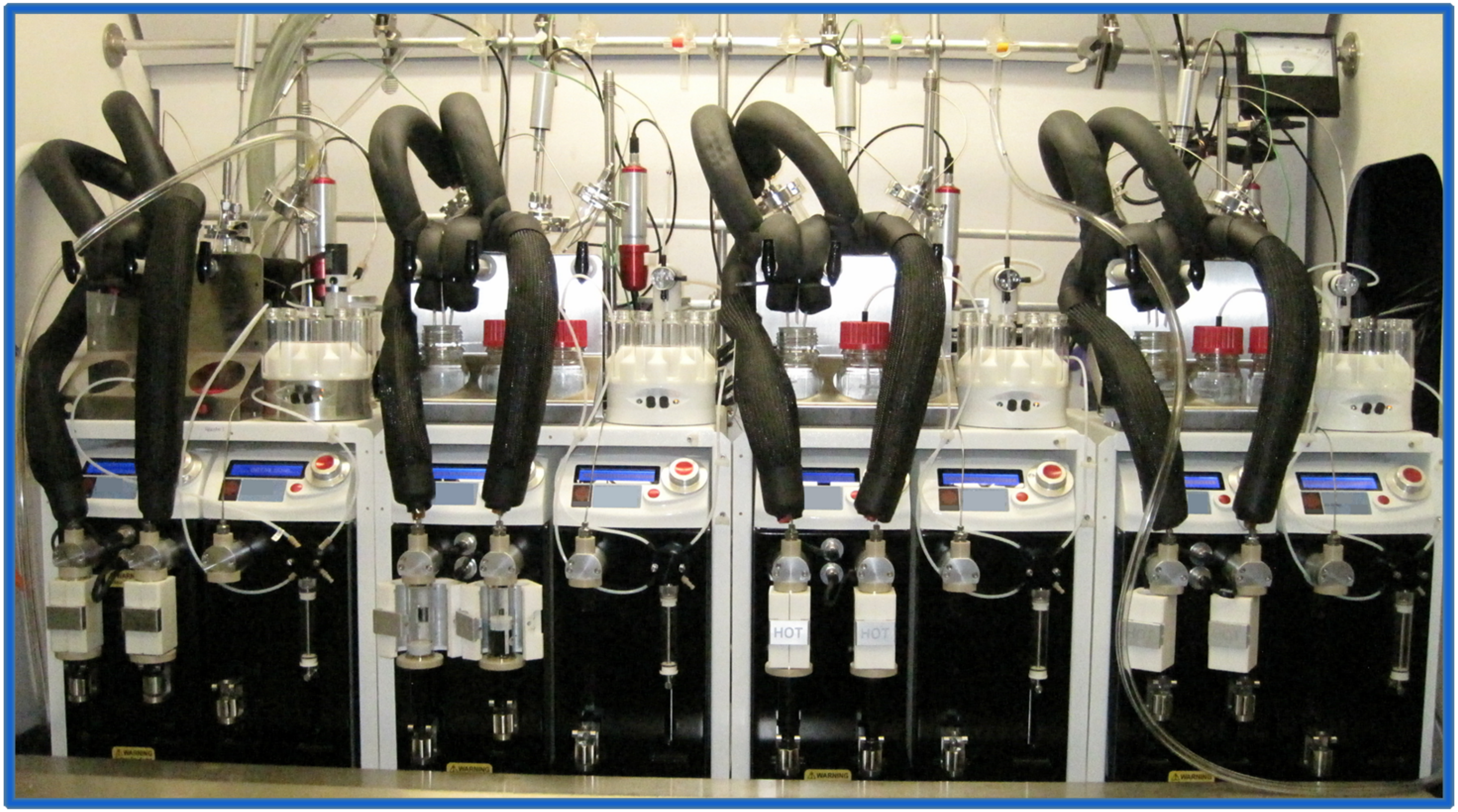
Accelerated lifetime testing (device-level)



Contacts: Jennifer Hollingsworth, jenn@lanl.gov and Han Htoon, htoon@lanl.gov (

Scale-up & reproducibility

Automated parallel reactor system



…designed to make multi-step synthetic processes scalable and reproducible