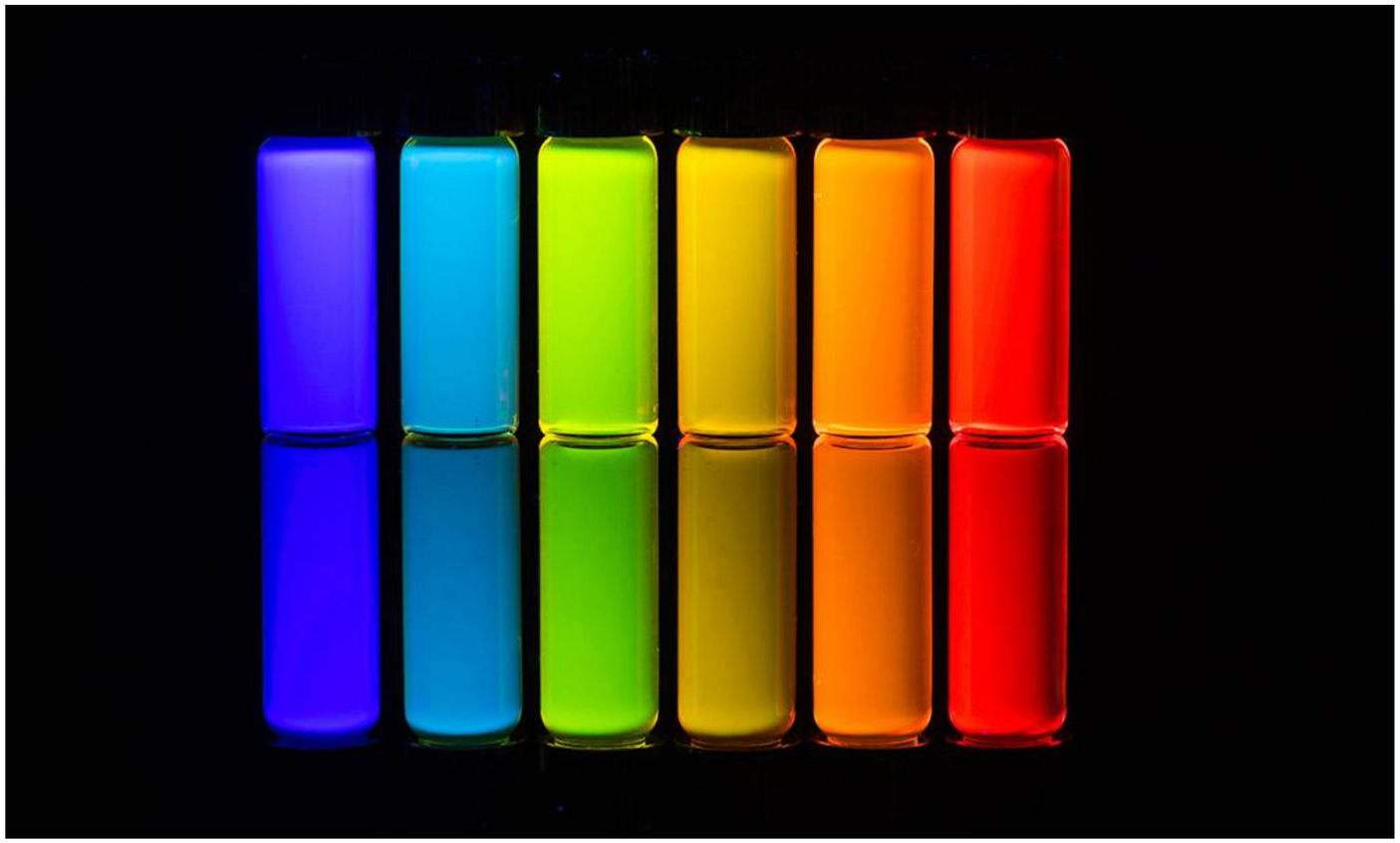
# *Quantum Dots: Applications in Energy and Electron Transfer Processes*



Gabrielle Lovett

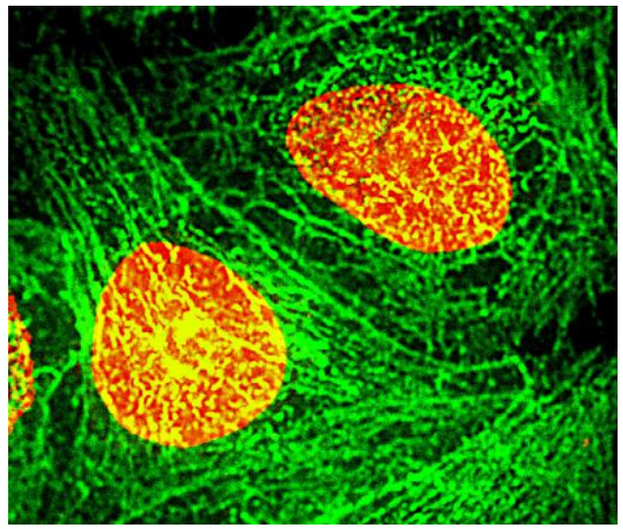
MacMillan Group Meeting

May 8, 2018

# *Introduction to Quantum Dots*

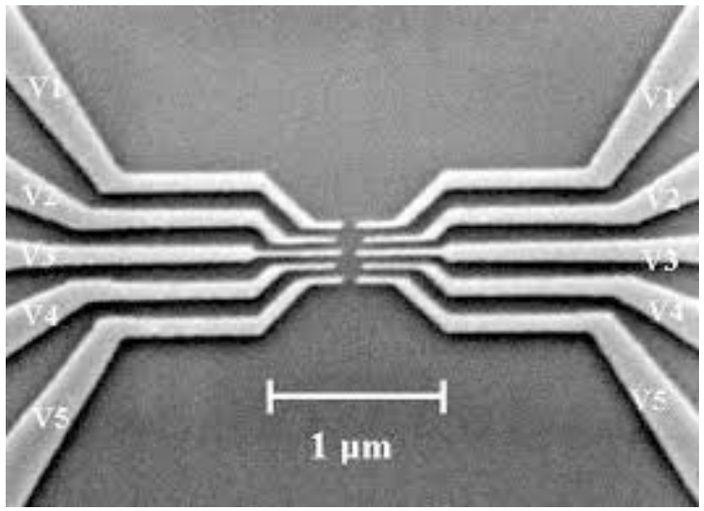
**Quantum Dots**: *semiconductor nanocrystals with tunable optical and electronic properties that differ from the bulk material due to size-dependent quantum confinement*


*QD-LEDs*



*bioimaging*

*photovoltaic devices*

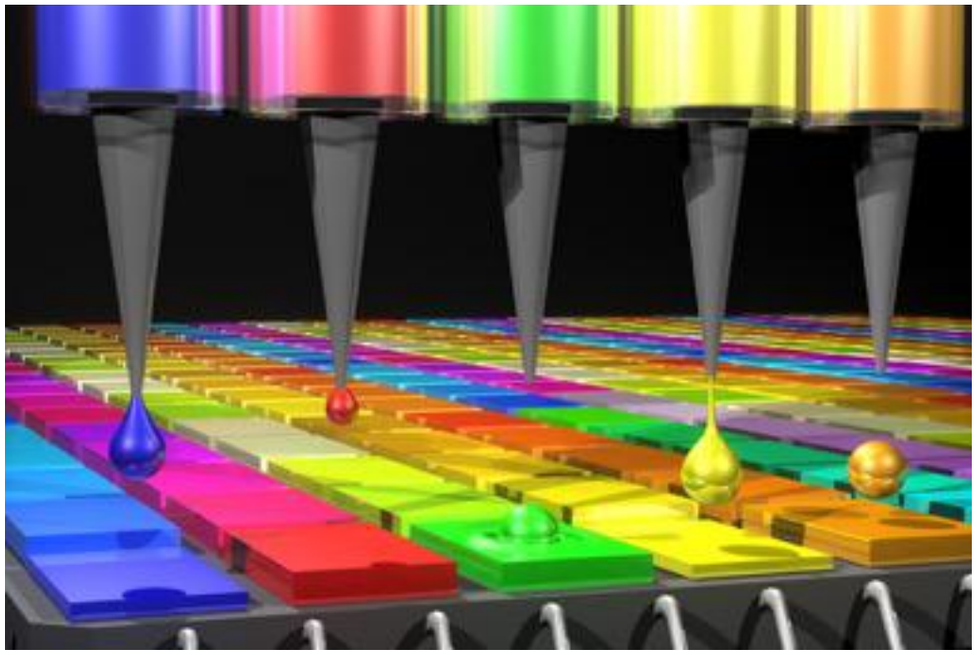



*quantum computing*

# *Outline*

- Background
  - quantum confinement
  - tunable optical properties
  - tunable electronic properties

- Applications in electron transfer processes
  - general mechanistic scheme
  - net reductive and oxidative reactions
  - QDs as photocatalysts in photoredox reactions
- Applications in energy transfer processes
  - general mechanistic scheme
  - applications in photovoltaics
  - applications in biological systems



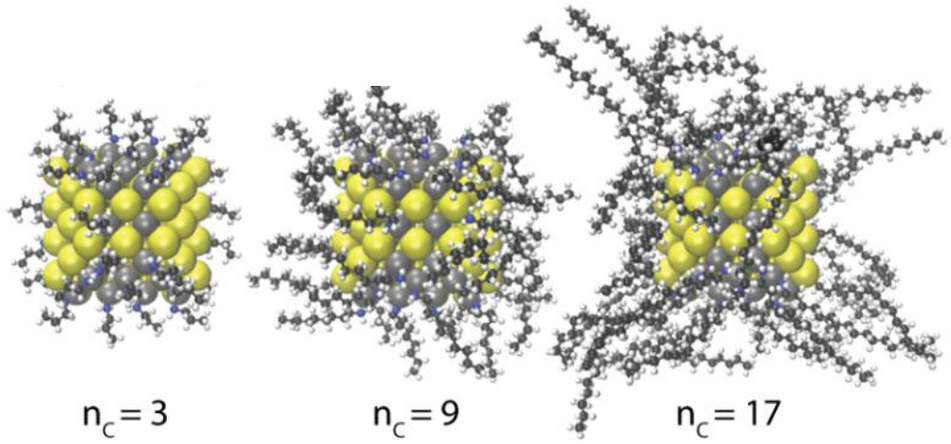
# *Introduction to Quantum Dots*

**Quantum Dots**: *semiconductor nanocrystals with tunable optical and electronic properties that differ from the bulk material due to size-dependent quantum confinement*

- solid quantum dot discovery in 1981 by Alexei Ekimov
- quantum dots in colloidal solutions discovered in 1983 by Louis Brus
- typically formed from groups II-VI (CdSe, ZnS) amd III-V (InAs, GaAs)

**Louis Brus**

- QDs possess tunable and size-dependent optical and electronic properties
- quantum dots are “artificial atoms” with properties between small molecule and bulk material

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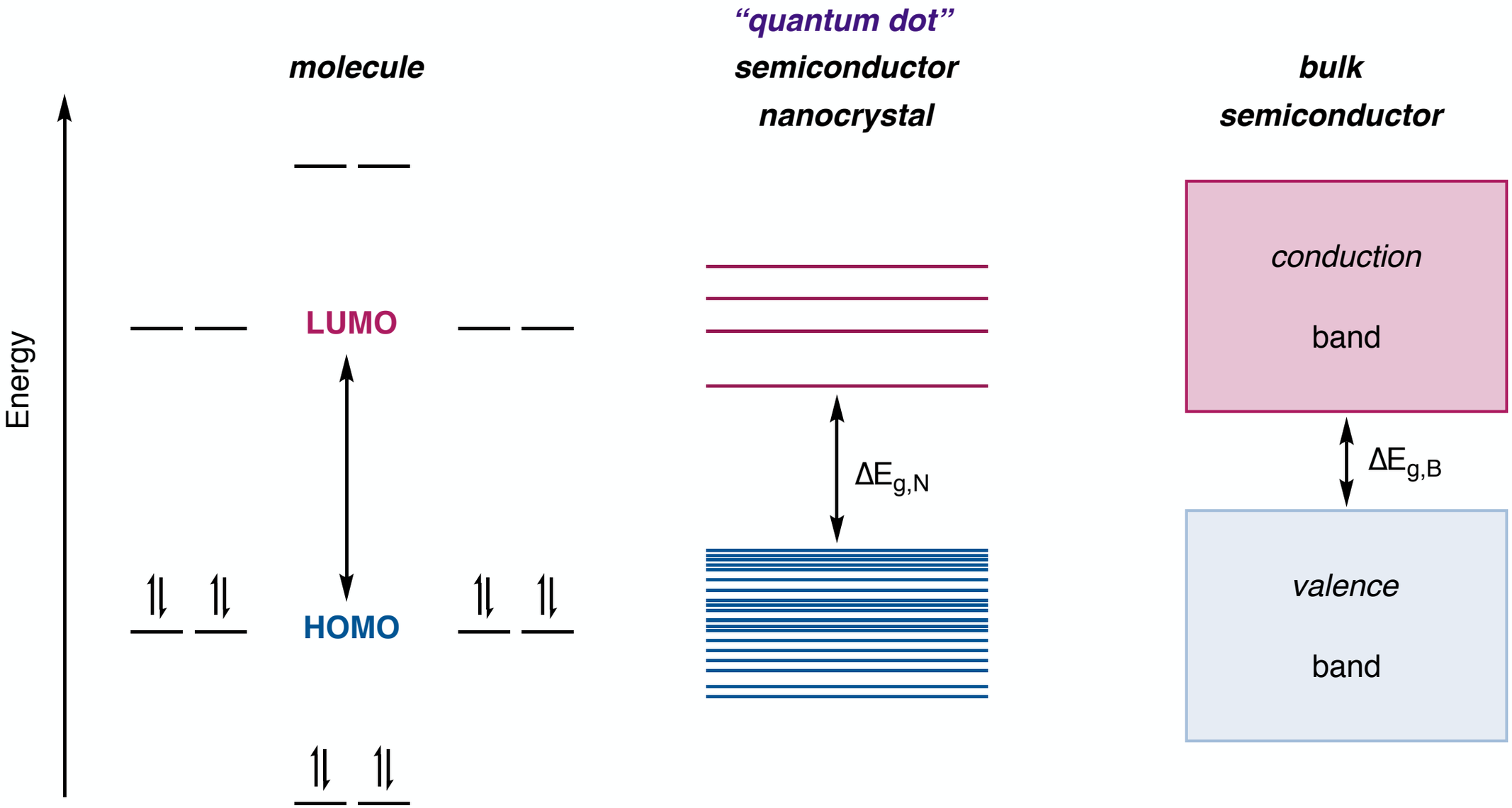
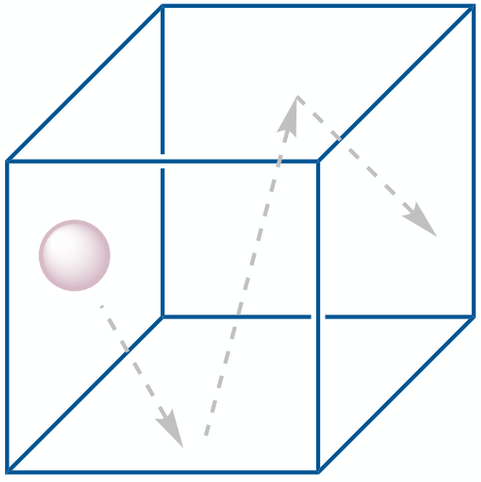



***as the radius of a semiconductor decreases to nanometer size, band gap energy increases***

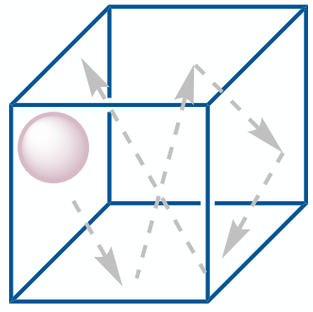
# *Introduction to Quantum Dots: Quantum Confinement*

- First, some definitions…
  - **exciton**: electrostatically bound electron–hole pair
  - **Bohr exciton radius**: the most-probable distance between the $e^-$ and hole within the exciton
    this is material-dependent (1 nm < r <100 nm)
  - **quantum confinement:** when the Bohr exciton radius exceeds the radius of the semiconductor sphere



*particle becomes spatially confined*

*raises particle energy*



**bulk semiconductor**

*exitons act as “free-particles”*

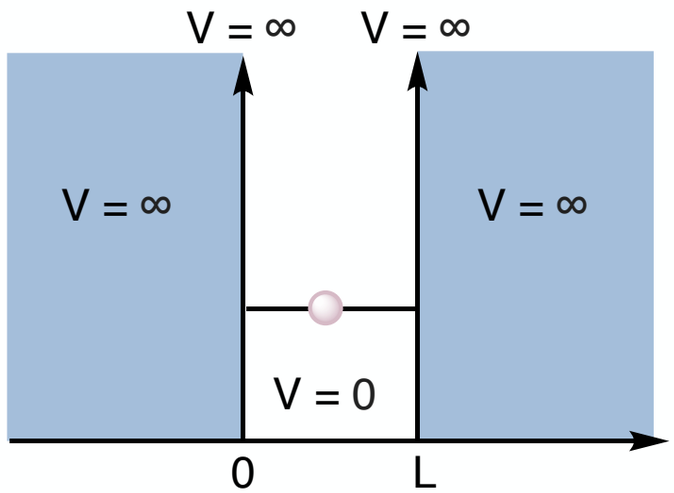
**semiconductor nanocrystal**

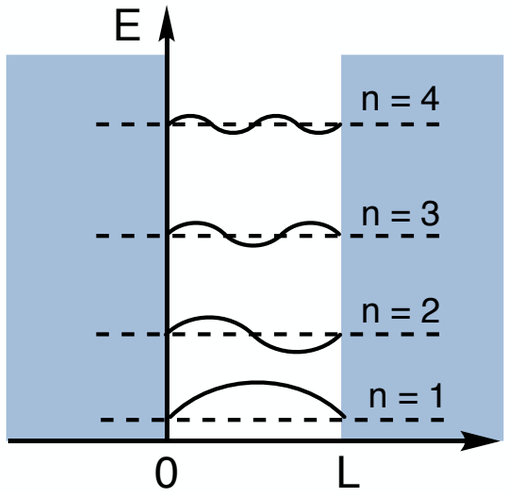
*exitons confined to box: boundary conditions*

***particle in a box!***

# *Particle in a Box Approximation*

## Particle in a Box 1D box




$$E_n = \frac{h^2 n^2}{8mL^2}$$

boundary conditions

leads to quantization of energy

## Extending this model to a 3D sphere (quantum dot)

$$\Delta E_r = E_{gap} + \frac{h^2}{8r^2}\left(1/m_e^* + 1/m_h^*\right)$$

$E_{gap}$ = band gap of the bulk material

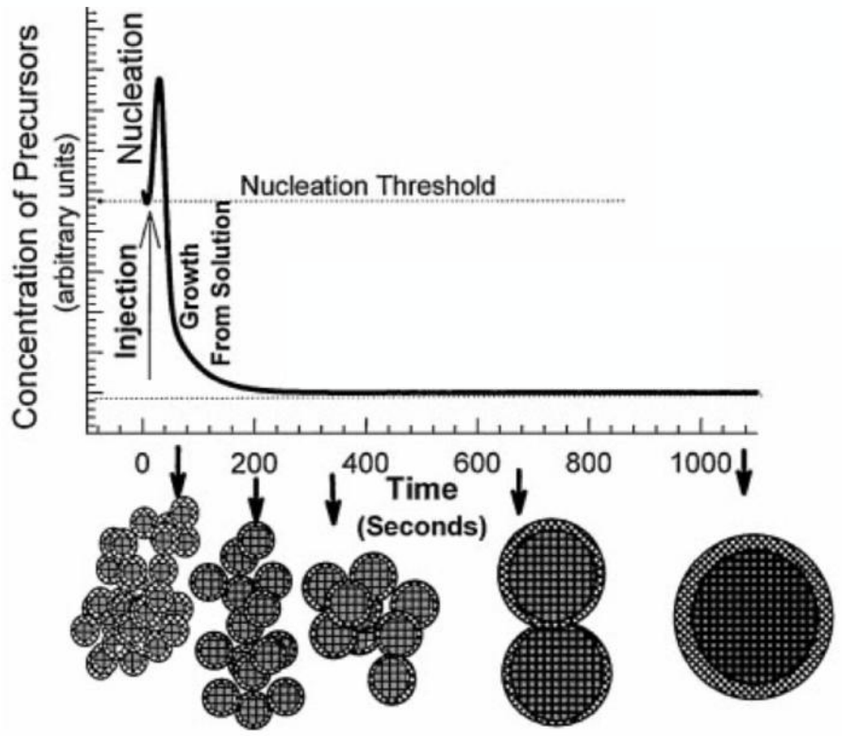
r = radius of the quantum dot

$m_{e/h}^*$ = effective mass of electron/hole

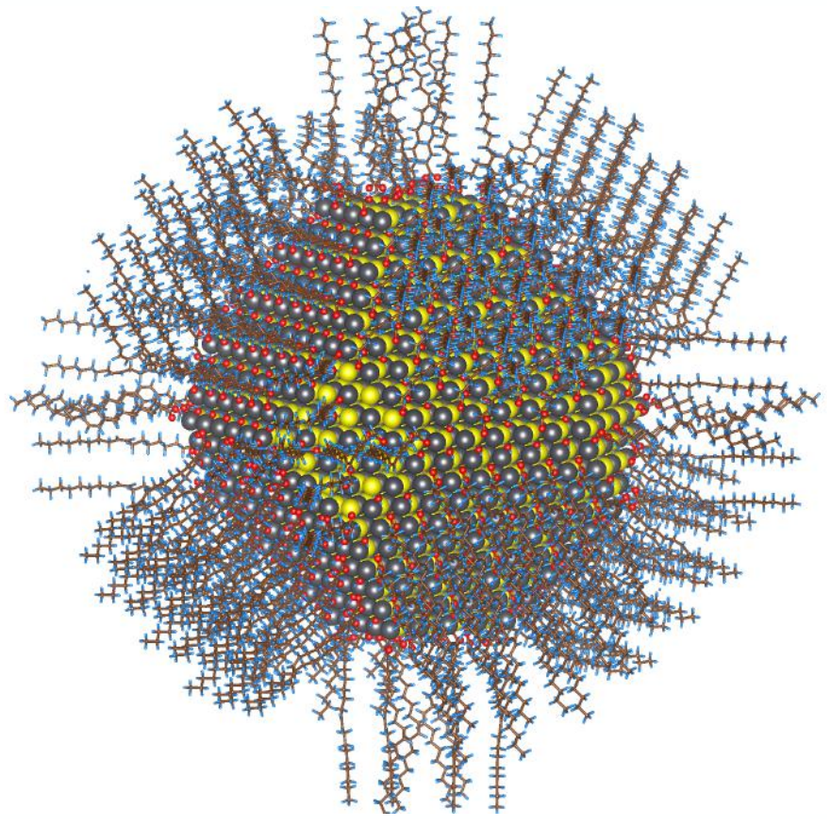
***size and wavelength of the quantum dot are directly proportional***

# *High-Temperature Colloidal Quantum Dot Synthesis: CdSe*

Monodisperse Colloid Growth (La Mer)




*increased particle size with time*



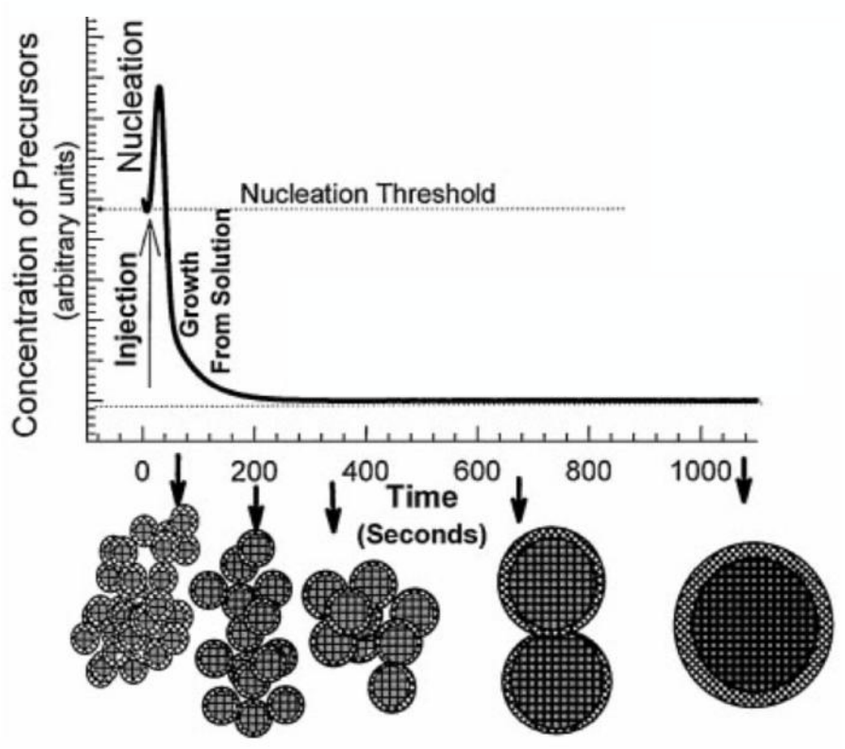
*QD with capping groups (ligands)*

- Rapid injection of precursor solutions into hot coordinating solvent - growth solution
- monodisperse nanoparticles can form if growth during nucleation period in minimized
- capping groups present during growth to prevent aggregation and preceiptation of QD

For review on colloidal QD synthesis on scale: *Ind. Eng. Chem. Res.* **2018**, *57*, 1790.
Murray, C.B.; Kagan C.R.; Bawendi, M.G. *Annu. Rev. Mater. Sci.*, **2000**, *30*, 545.

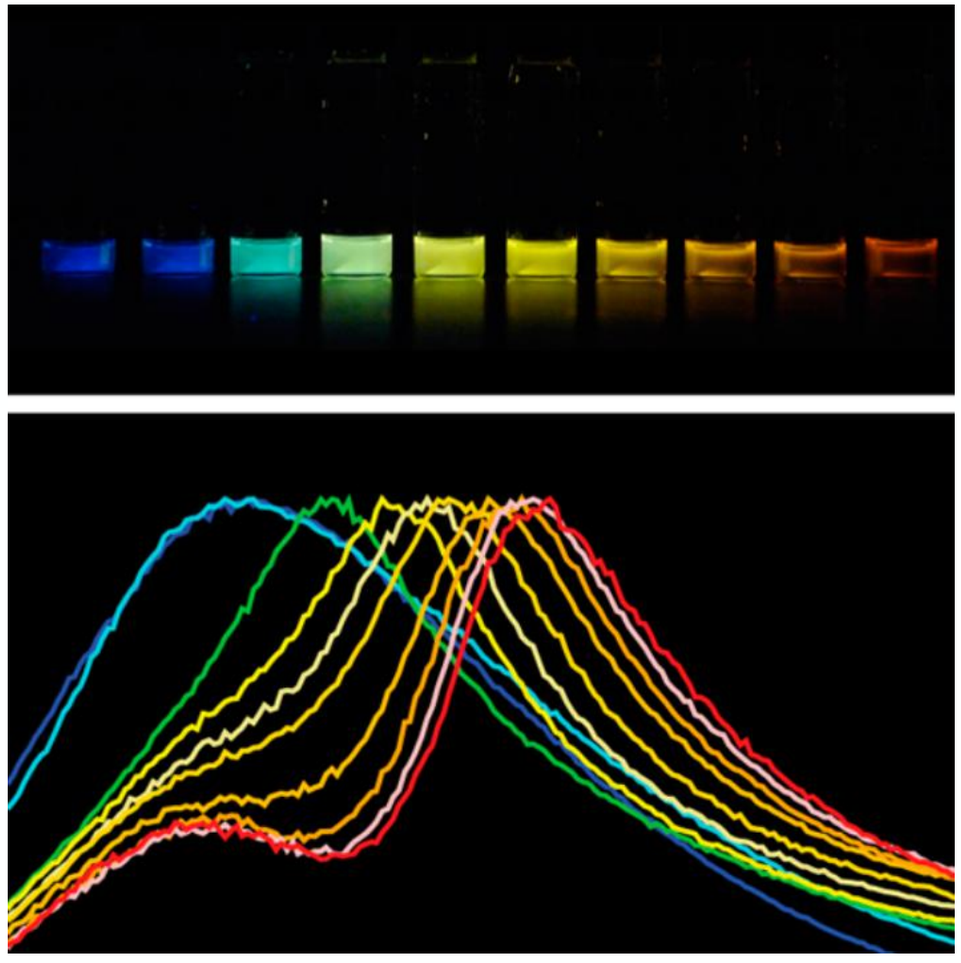
# *Relationship Between QD Size and Optical Properties*

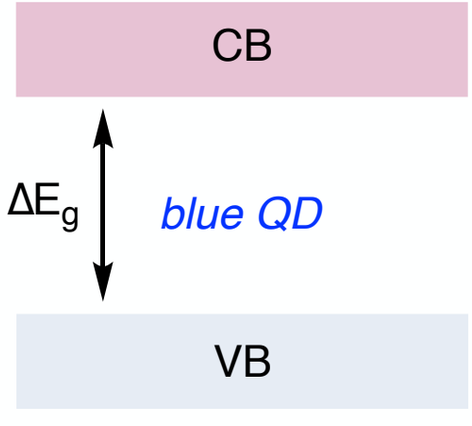
Monodisperse Colloid Growth (La Mer)

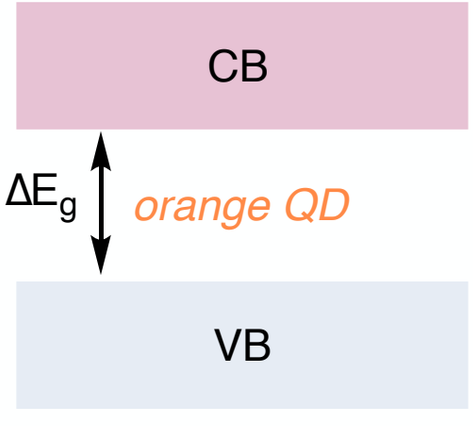


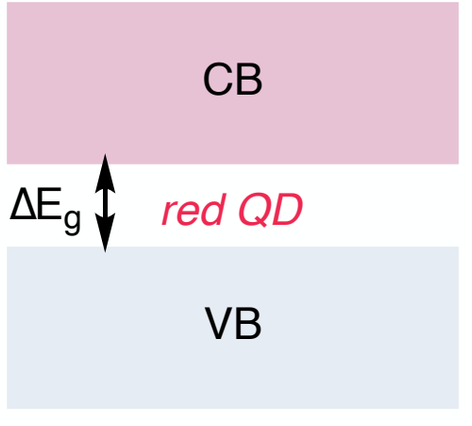

*increased particle size with time*

*increase in wavelength, decrease in $\Delta E_g$*



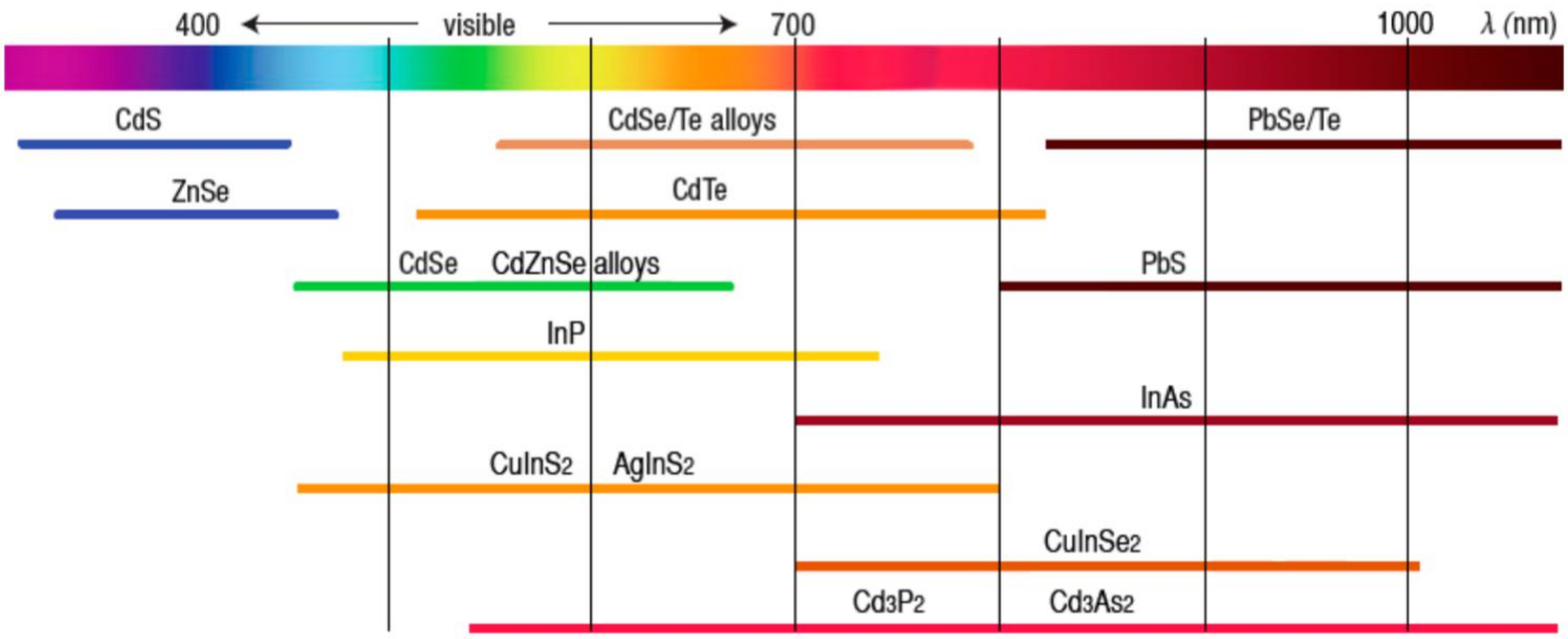


# *Relationship Between QD Size and Optical Properties*

- *Different QD's have different characteristic band gaps spanning UV to IR absorption*

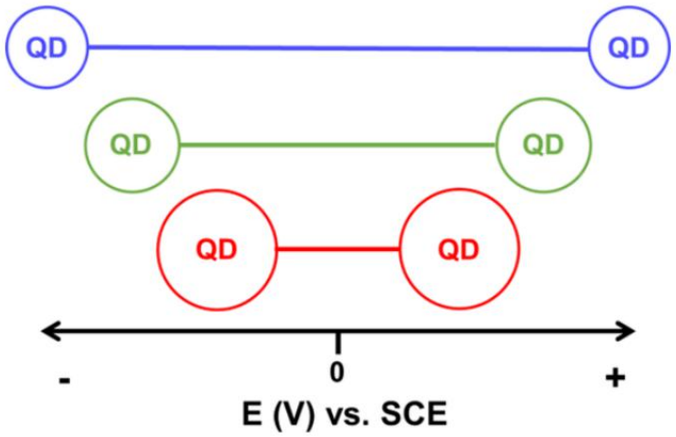


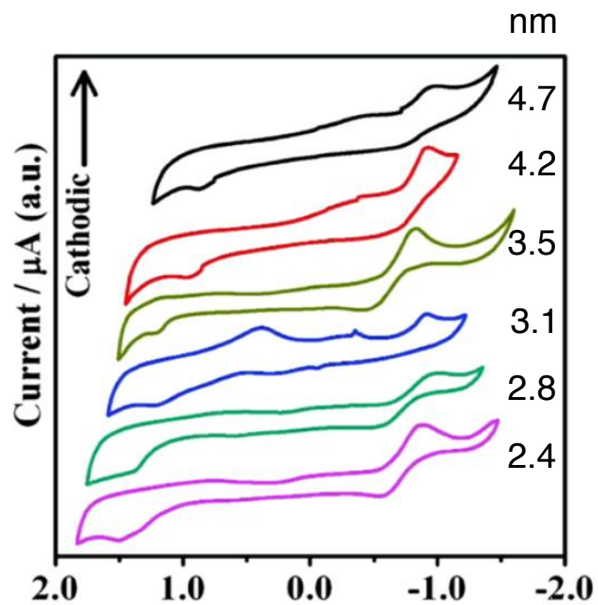

***what is the relationship between QD optical bandgap and its electrochemical bandgap?***

Tamang. S. et el. *Chem. Rev.* **2016**, *116, 10731.*

# *Relationship Between QD Size and Electrochemical Potential*

- *Tuning QD size alters the bandgap electrochemical potentials*




- *Relationship between electrochemical bandgap and optical bandgap*

$$\Delta E_{g,opt} = \Delta E_{g,el} - J_{e,h}$$

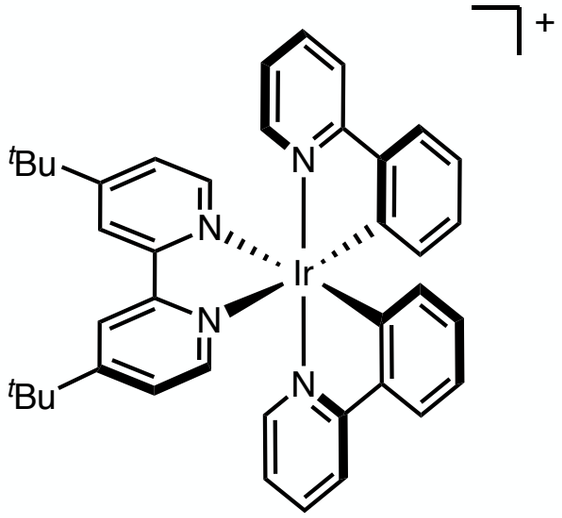
*where $J_{e,h}$ is the stabilizing electron-hole binding energy*

***both absorption wavelength and redox window of QD's are highly tunable***

For comprehensive list of QD electrochemical potenials, see: *Chem. Rev.* **2016**, *116*, 12865.

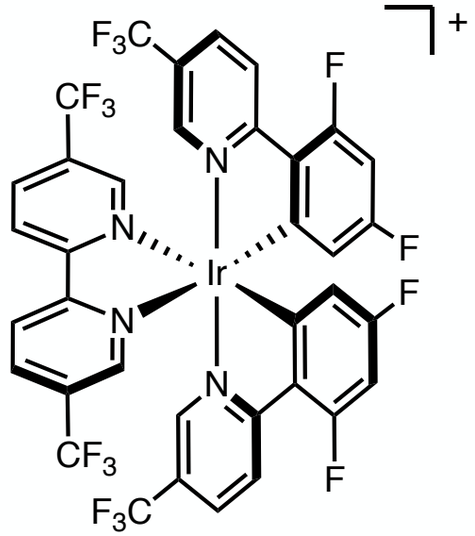
# *QD Ligand Effect on Electrochemical Window*

- *Analogy to Ir photocatalysts: electronics of ligands shift redox window*




**Ir(III)*/Ir(II) = 0.66 V**

**Ir(III)/Ir(II) = -1.51 V**




**Ir(III)*/Ir(II) = 1.68 V**

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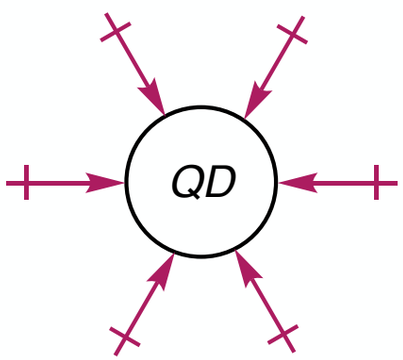
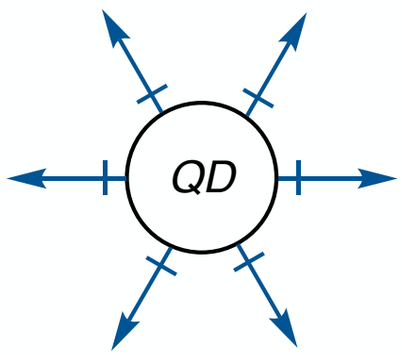
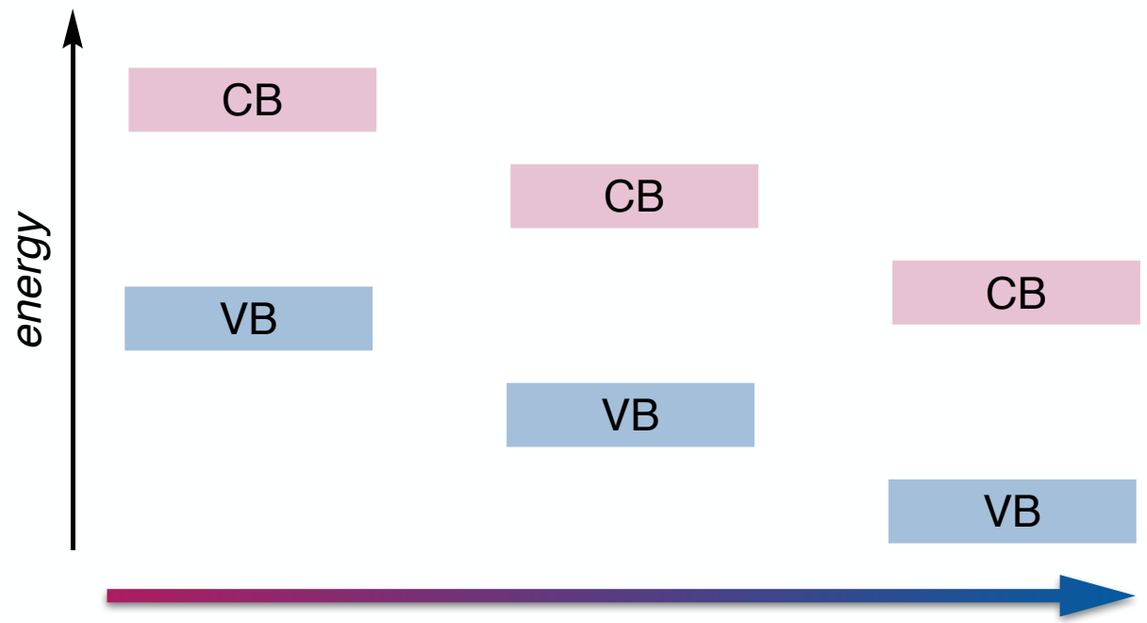
- *Tuning the dipole moment of QD-ligand interface has similar effect*




*donating ligands*




*withdrawing ligands*

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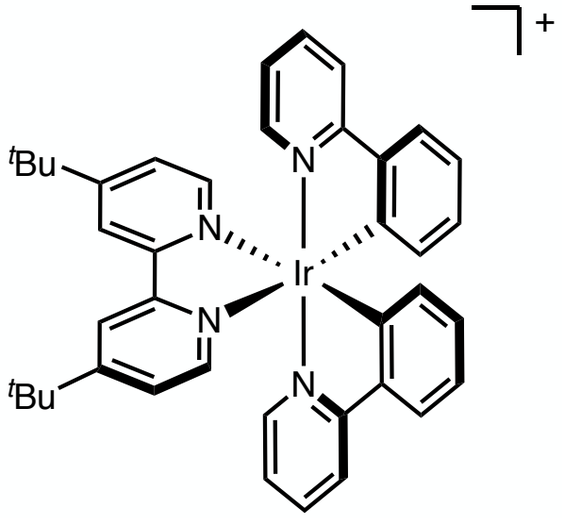


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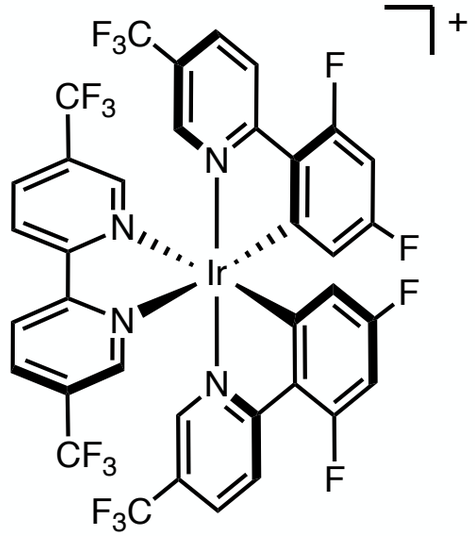


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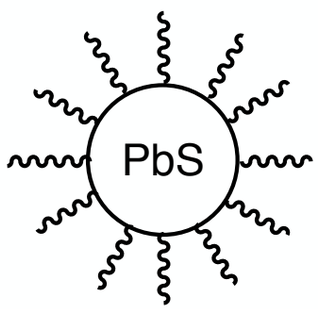
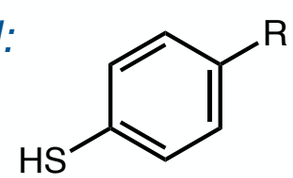
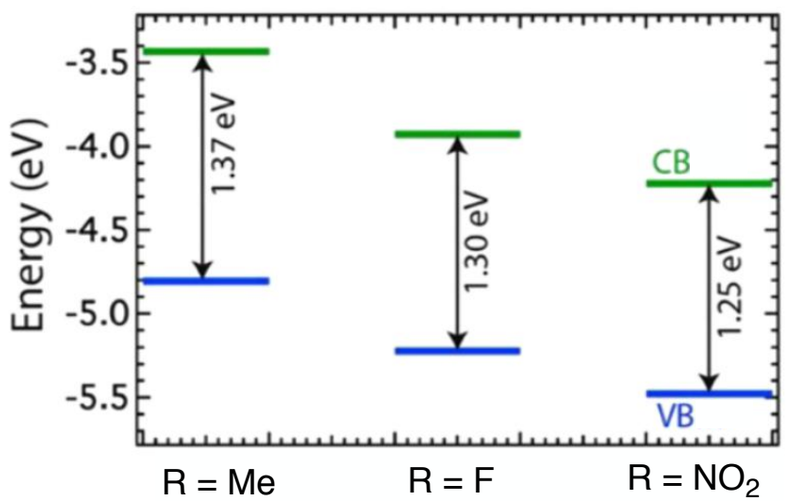
*QD:*




*Ligand:*




For comprehensive list of redox windows of various QD's and ligands, see:

*Chem. Rev.* **2016**, *116*, 12865.

Bent, S.F. *J. Phys. Chem. C.* **2015**, *119*, 2996.

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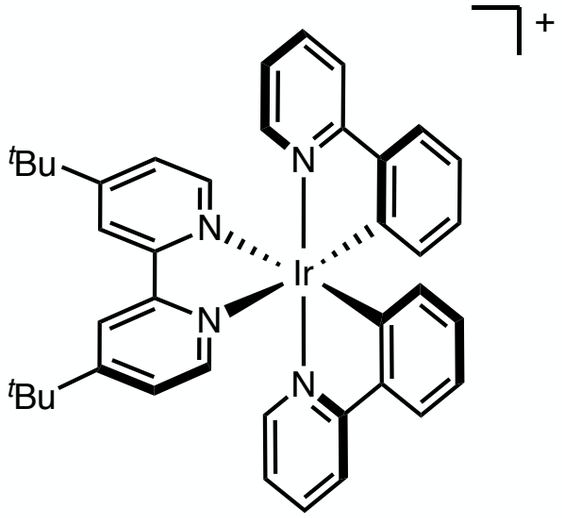


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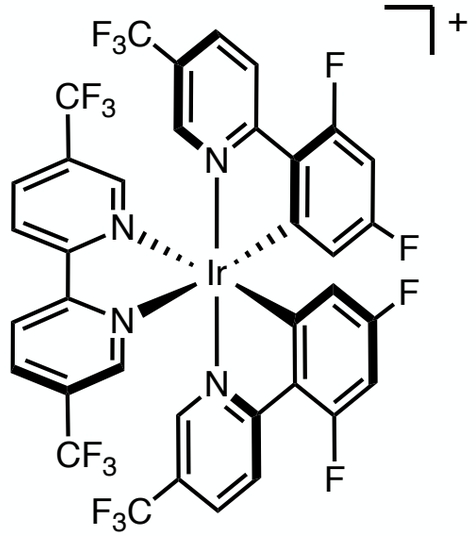


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- *Tuning the dipole moment of QD-ligand interface has similar effect*

***bandgap shifts as large as 0.9 eV have been reported***

**as ligands tuned from highly donating to highly withdrawing**

For comprehensive list of redox windows of various QD's and ligands, see:

*Chem. Rev.* **2016**, *116*, 12865.

*ACS Nano*, **2014**, *8*, 5863.

Bent, S.F. *J. Phys. Chem. C.* **2015**, *119*, 2996.

# *QDs as Ideal Photocatalysts*

- Comparison of triple excited state of Ir photocatalyts and QDs

| ***Typical Ir Photocatalysts:*** | ***Quantum Dots:*** |
|---|---|
| initially excited to singlet | ill-defined spin quanta: mixed spin character |
| interstystem crossing to triplet, loss of energy | avoid energetic loss from intersystem crossing to triplet |
| **Ir photocatalysts, on order of $10^2$ meV** | **For CdSe, excited state spacing 1–15 meV** |

***properties of quantum dots***

- *small Stokes shift*
- *photostable*
- *high molar extinction coefficients*
- *broad absorption spectrum*
- *readily synthesized*
- *highly tunable properties*

***ideal photocatalyst properties***

*Adv. Funct. Mater.* **2008**, *18,* 1157.
Inorg. Chem. **2018**, *57*, 2351

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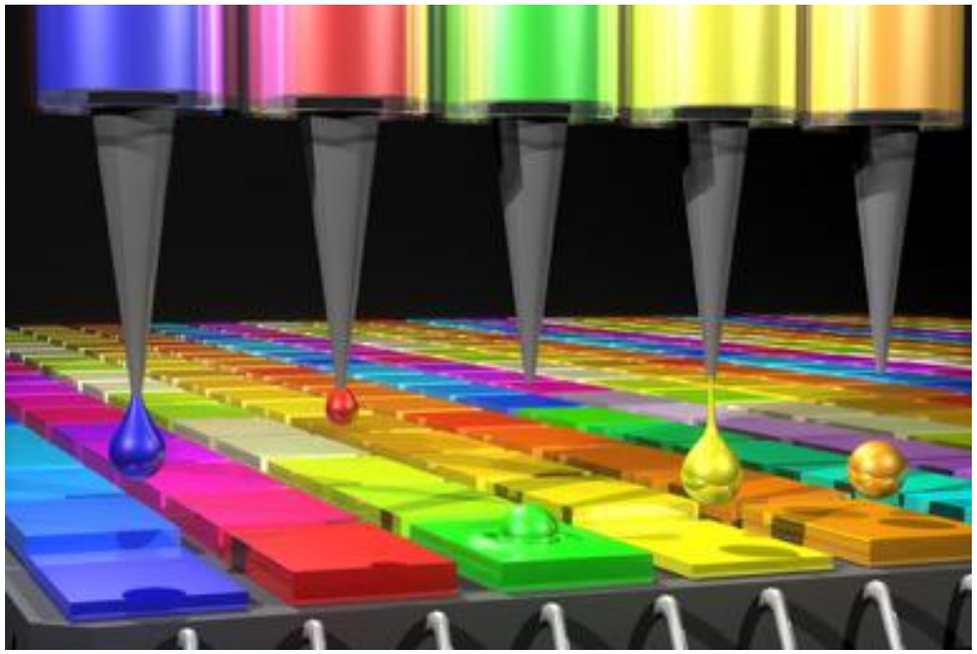
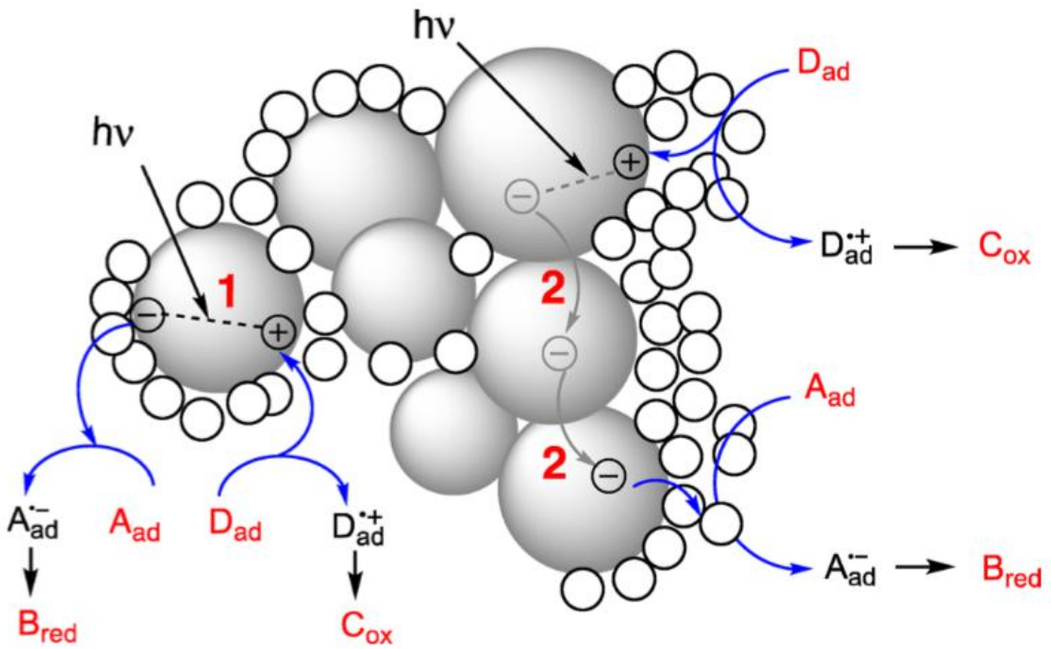
  - quantum confinement
  - tunable optical properties
  - tunable electronic properties

- *Applications in electron transfer processes*
  - general mechanistic scheme
  - net reductive and oxidative reactions
  - QDs as photocatalysts in photoredox reactions
- *Applications in energy transfer processes*
  - general mechanistic scheme
  - applications in photovoltaics
  - applications in biological systems



# *QDs in Photocatalysis: General Mechanism*

## Model for QD Photocatalysis

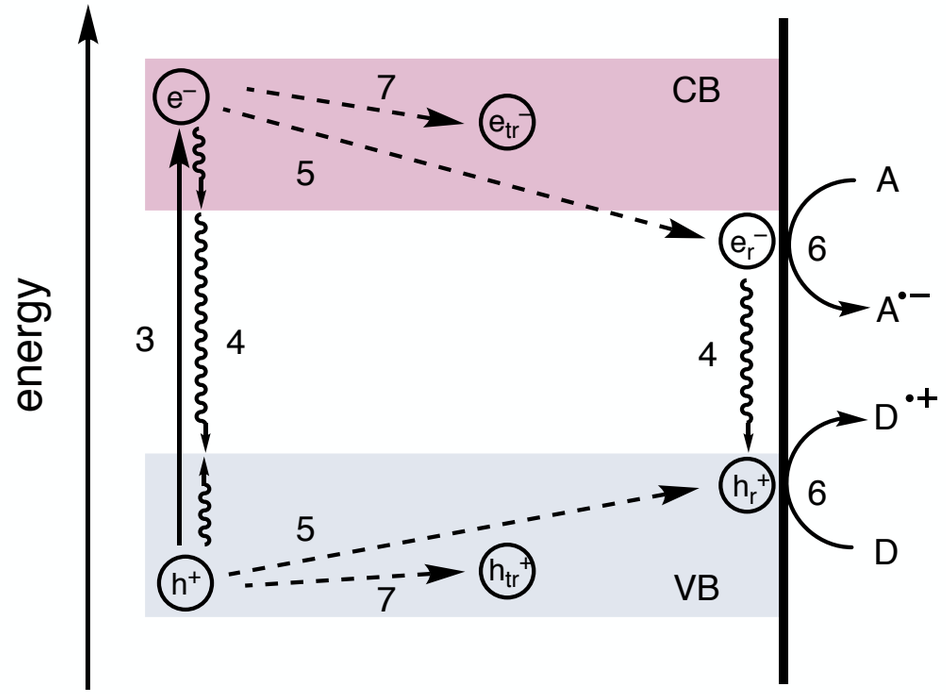



*1: charge transfer occurs on single crystal*

2: intercrystallite electron transfer

*improved efficiency of formation of reactive $e^-$-$h^+$*

## Generation of Reactive Species: Simplified View




*3: photoexcitation to generate $e^-$-$h^+$ pair*

*4: charge recomination*

*5: migration to surface: reactive species*

*6: electron transfer*

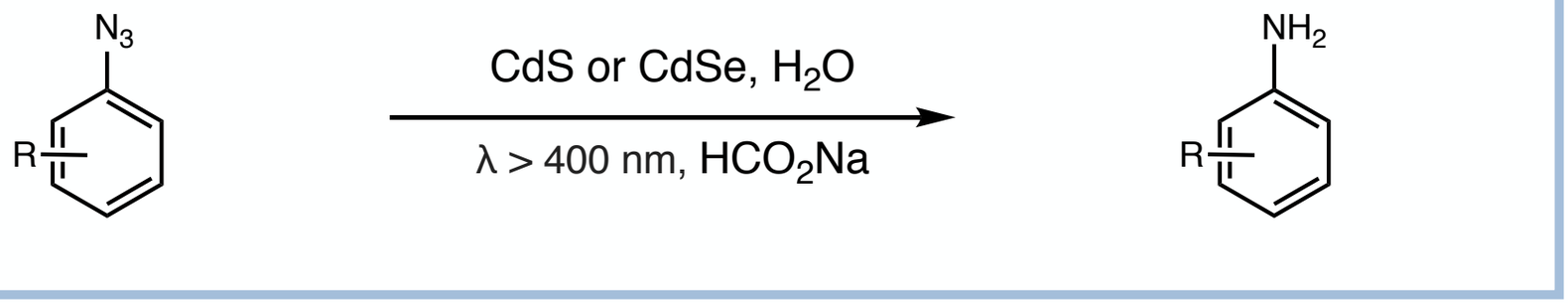
*7: migration to surface: dissociatively trapped*

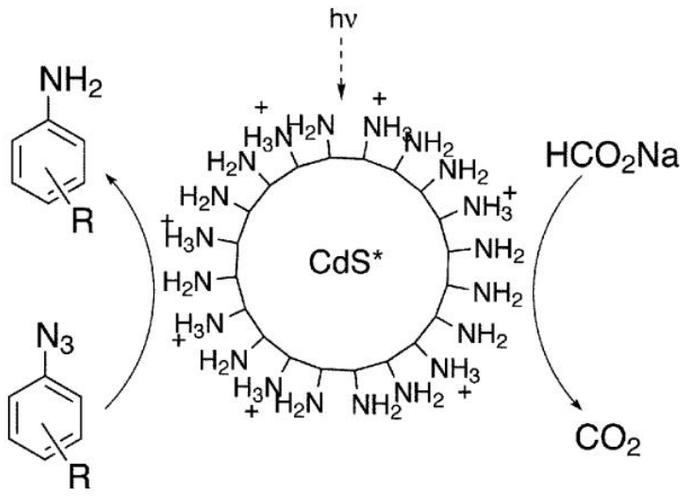
**excited-state energy in QDs is dissipated over entire nanocrystal: little change from GS structure**

*J. Am. Chem. Soc.* **2017**, *139*, 3302.
*Acc. Chem. Res.* **2017**, *50*, 1002.

# *QDs in Photocatalysis: Early Applications*

- Early applications were net oxidative or reductive, requiring sacrificial $e^-$ donors or acceptors
- $CO_2$ reductions catalyzed by ZnS QDs were reported in the 90's
- CdSe or CdS catalyzed reduction of aromatic azides (2004)




estimated photoexcited 2 nm CdS potential ~ – 1.5 V vs. SCE

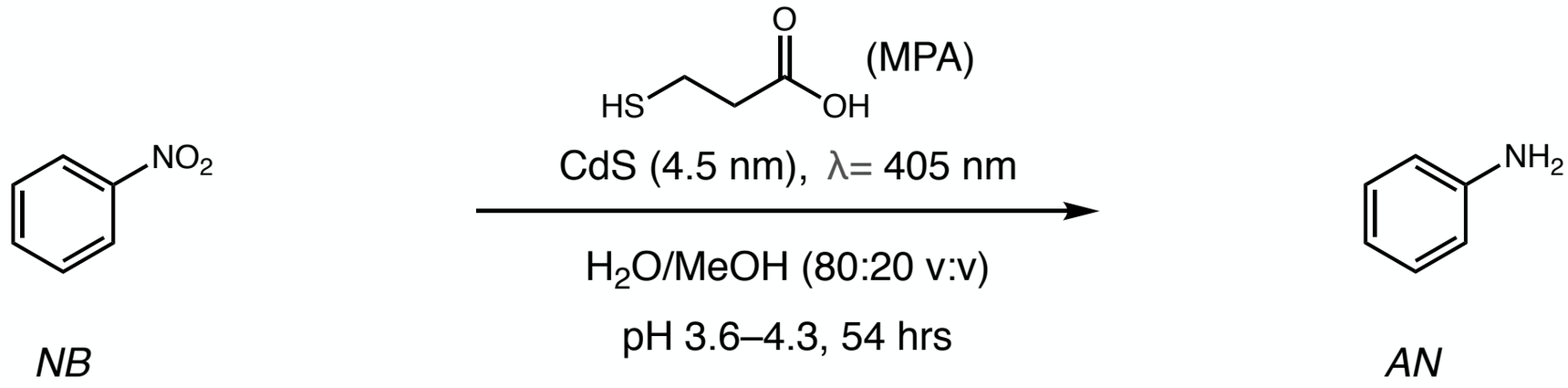
sodium formate as sacrificial reductant

aminethiol ligands: nanoparticle surface postively charged at neutral pH

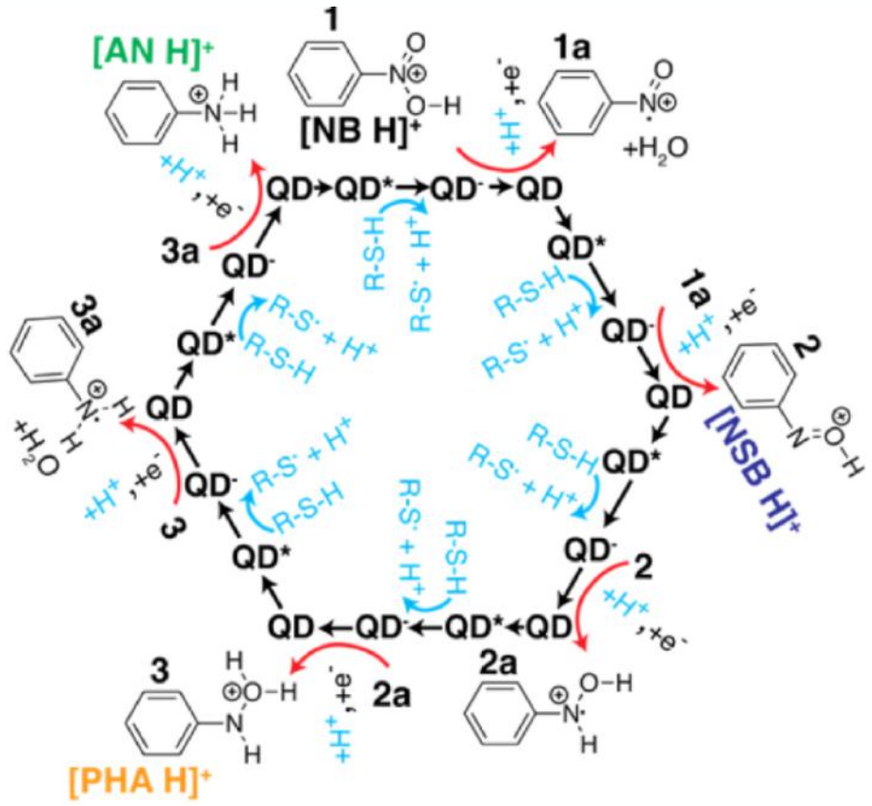
*Photochem. Photobiol. Sci.* **2004**, *3*, 859
*Chem. Lett.* **1990**, 1483
*Catal. Today* **1997**, *39,* 169.

# *QDs in Photocatalysis: Multi-Electron Reductions*

- Conversion of nitrobenzene to aniline




- Proposed catalytic cycle for $6e^-$, $6H^+$ process




*MPA acts both as acid and as reductant*

*acidic pH critical for protonation of the final product*

*aniline can bind to QD surface, poisoning the catalyst*

| | no MPA (pH ~9) | | 15 mM MPA (pH ~5) | |
|---|---|---|---|---|
| | molecules bound per QD | $K_{ads}$ = [bound]/[free] | molecules bound per QD | $K_{ads}$ = [bound]/[free] |
| NB | 80.5 ± 8.9 | 0.81 ± 0.09 | 80.3 ± 1.2 | 0.80 ± 0.01 |
| AN | 82.1 ± 2.2 | 0.82 ± 0.02 | 13.5 ± 2.4 | 0.13 ± 0.02 |

*J. Am. Chem. Soc.* **2016**, *138*, 1591.

# *QDs in Photocatalysis: Multi-Electron Reductions*

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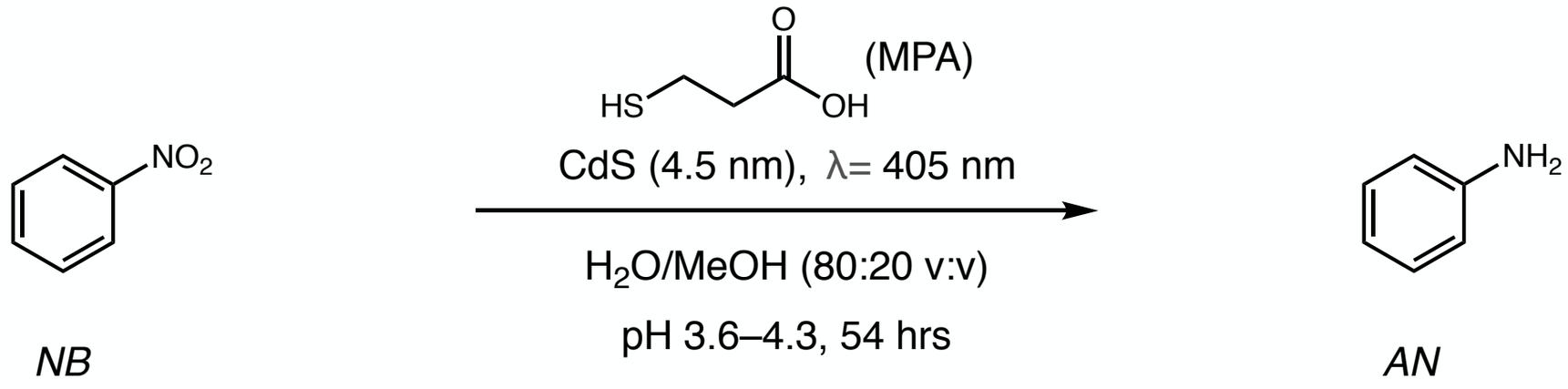
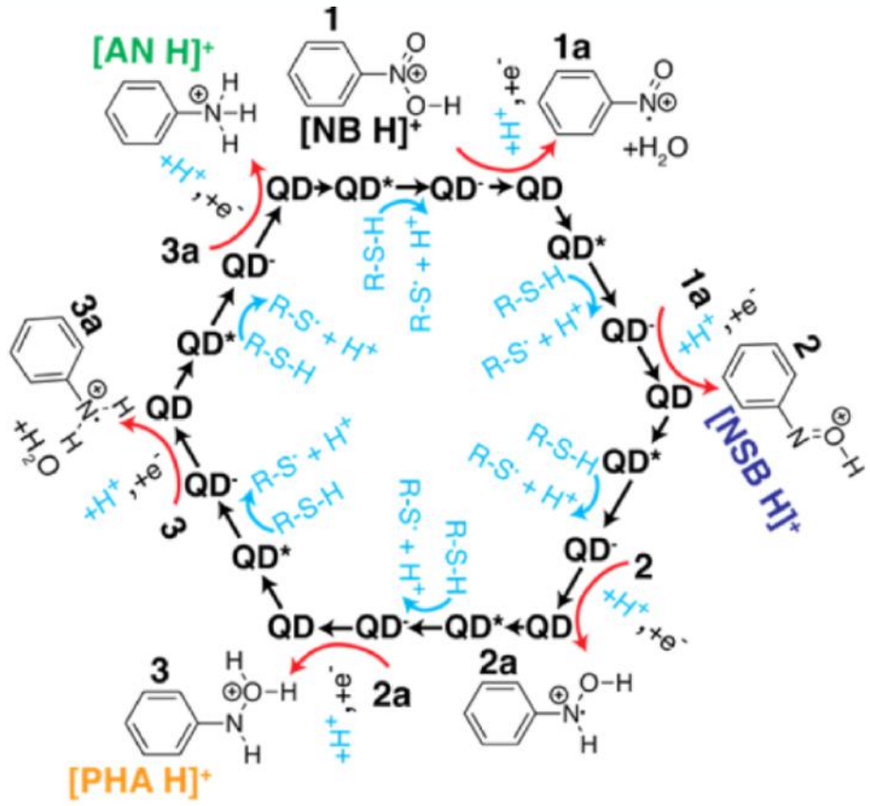



- Proposed catalytic cycle for $6e^-$, $6H^+$ process




*adsorption of reagents and intermediates on QD surface*

↓

*reaction not under diffusion-controlled conditions*

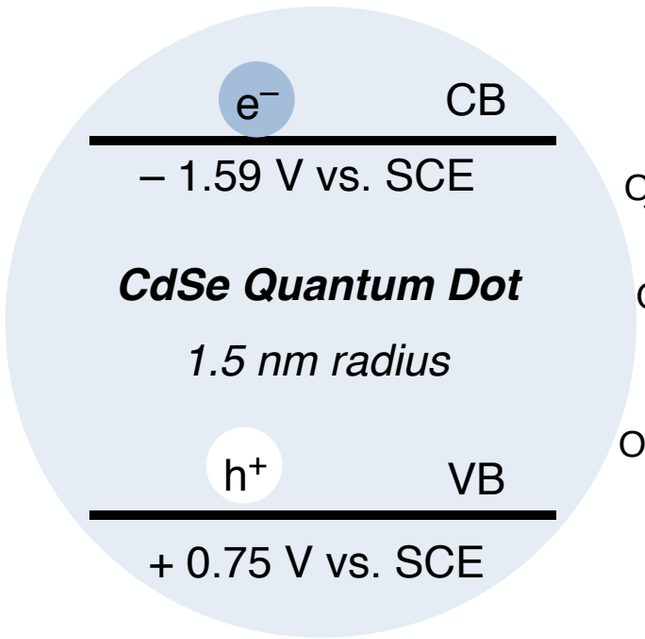
| | no MPA (pH ~9) | | 15 mM MPA (pH ~5) | |
|---|---|---|---|---|
| | molecules bound per QD | $K_{ads}$ = [bound]/[free] | molecules bound per QD | $K_{ads}$ = [bound]/[free] |
| NB | 80.5 ± 8.9 | 0.81 ± 0.09 | 80.3 ± 1.2 | 0.80 ± 0.01 |
| AN | 82.1 ± 2.2 | 0.82 ± 0.02 | 13.5 ± 2.4 | 0.13 ± 0.02 |

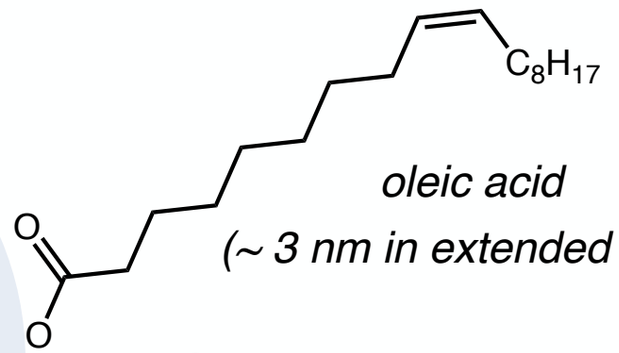
*J. Am. Chem. Soc.* **2016**, *138*, 1591.

# *QDs in Photoredox Catalysis*

- Can CdSe QDs be used in place of Ru or Ir photocatalysts?

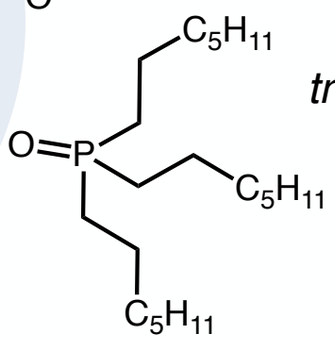
| | | |
|---|---|---|
| **catalyst** | **$Ir(ppy)_2(dtbbpy)PF_6$** | **CdSe QD** |
| **excited state reduction potentials** | ~ 1.51 V vs. SCE | ~ –1.43 to 1.80 V vs. SCE |
| **LEDs typically used** | **blue LEDS**: ~ 420 nm | **green LEDs**: ~ 530 nm |
| **molecular weight** | ~ $10^3$ | 8.8 x $10^4$ (including capping ligand) |
| **typical catalyst loadings** | ~ 1 mol% | ~ $10^{-3}$ mol% |




*oleic acid*

*(~ 3 nm in extended form)*




*trioctyl phosphine oxide*

*(~ 1.4 nm)*

*without reoptimization,*

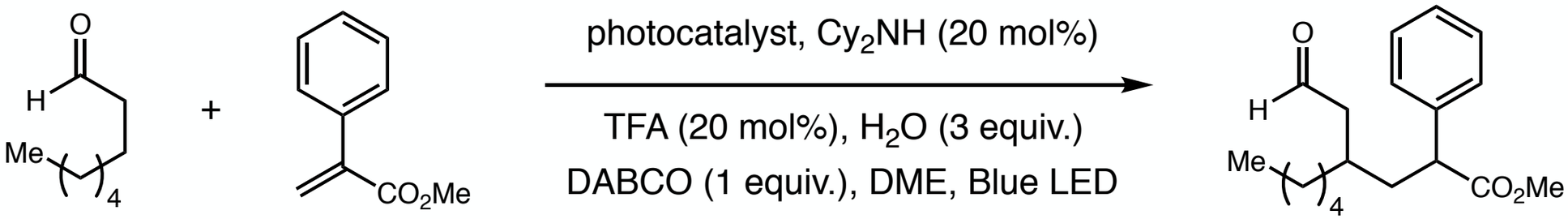
*can CdSe QDs*

*replace an Ir photocatalyst?*

*J. Am. Chem. Soc.* **2017**, *139*, 4250.

# *QDs in Photoredox Catalysis*

- Testing CdSe QD on a model photoredox reaction: β-alkylation




| photocatalyst | loading | yield | |
|---|---|---|---|
| $Ir(dmppy)_2(dtbbpy)PF_6$ | 1 mol% | 77% | *(optimized literature yield)* |
| CdSe QD (4.5 nm) | 0.0043 mol% | 12% | |
| CdSe QD (3.4 nm) | 0.0088 mol% | 63% | |
| CdSe QD (3.0 nm) | 0.0086 mol% | 67% | |
| CdSe QD (3.0 nm) | 0.00081 mol% | 64% | |
| CdSe QD (2.8 nm) | 0.0049 mol% | 70% | |
| $Ir(ppy)_2(dtbbpy)PF_6$ | 0.0031 mol% | 72% | |

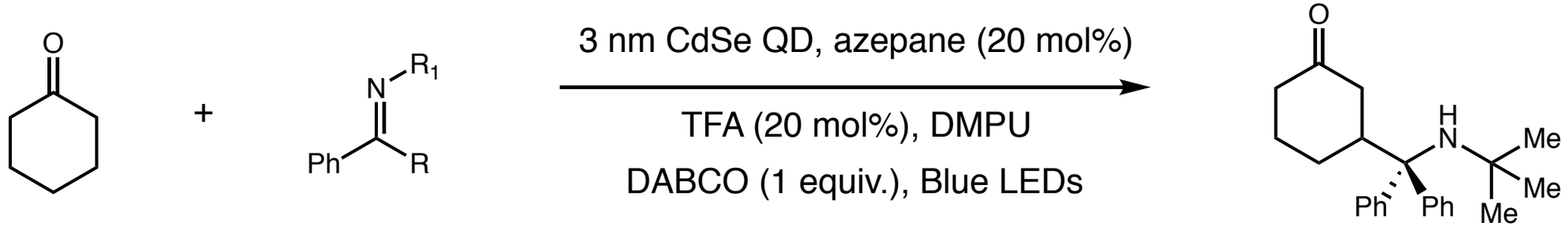
- *equivalent reaction efficiency with blue and green LEDs*
- *similar reaction efficiency at catalyst loadings of 0.0008 mol%*

*J. Am. Chem. Soc.* **2017**, *139*, 4250.

# *QDs in Photoredox Catalysis*

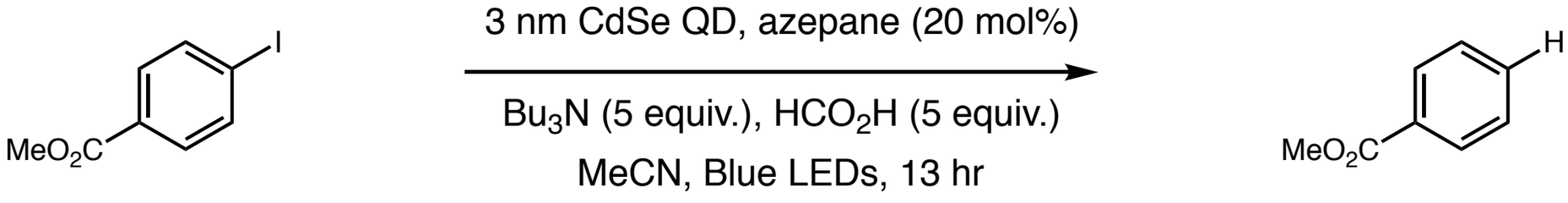
- Testing generality of CdSe QD in a variety of photoredox reactions

  - β-aminoalkylation




***90% yield***

  - reductive dehalogenation



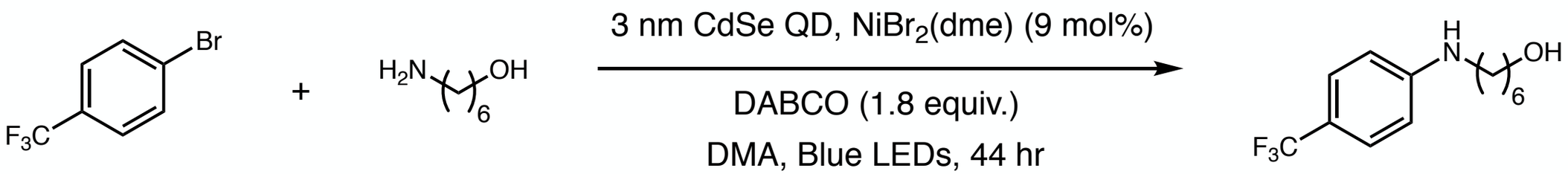

***93% yield***

***literature yields reproduced without need for reoptimization***

*J. Am. Chem. Soc.* **2017**, *139*, 4250.

# *QDs in Photoredox Catalysis*

- Testing generality of CdSe QD in a variety of photoredox reactions
  - amination




***58% yield***

- *literature yields generally reproduced without need for reoptimization*
  - *both organic and transition metal co-catalysts tolerated*
- *toleration of potential QD poisons, including: amines, alcohols, carboxylates*

*J. Am. Chem. Soc.* **2017**, *139*, 4250.

# *QDs in Photoredox Catalysis*

- Still room for improvement…
  - QDs used were 3 nm CdSe with oleate/TOP in octadecene
    - not reducing enough to replace $Ir(ppy)_3$ as photocatalyst
    - low quantum yield (0.31% for β-alkylation)
      - fast radiative recombination of $e^-h^+$ pair, non-radiative decay
    - issues with capping ligand stability
      - required oleic acid to stabilize QD
    - QD decomposition or aggregation observed in some cases

***possible solutions***

***Tunable redox properties:*** *reduction potentials up to – 2.4 vs. SCE for $CuInS_2$ QD*
*oxidation potentials up to + 1.9 vs. SCE for CdS QD*

***Tunable capping ligands:*** to alter solubility, permeability of ligand for substrate adsorption

***Extending excited-state lifetime:*** "core-shell" QDs CdSe/ZnSe QD (lifetime on *μ*s scale)

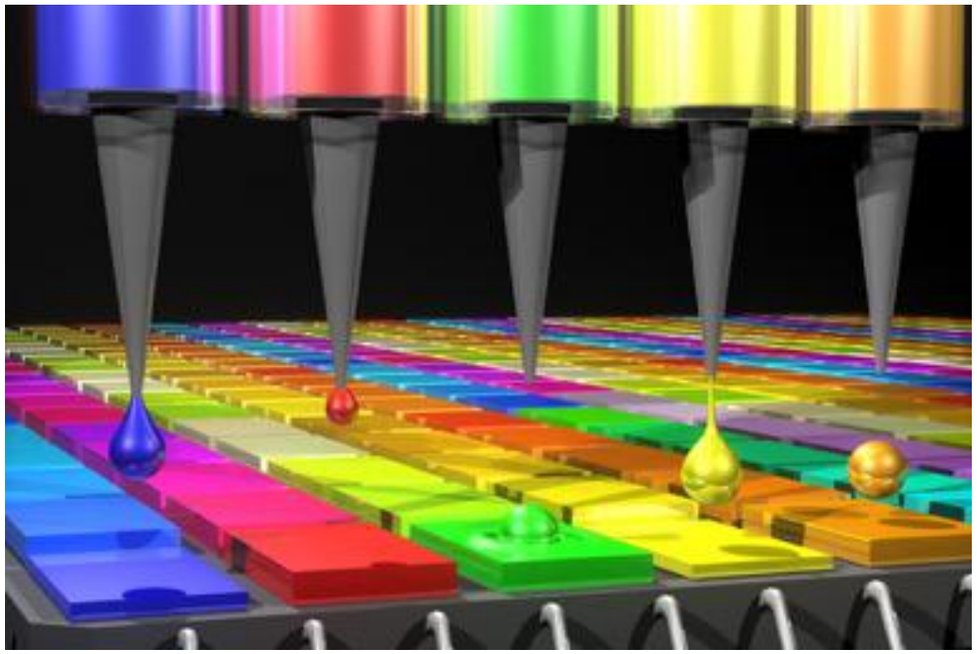
*Inorg. Chem.* **2018**, *57*, 3659.
*J. Am. Chem. Soc.* **2017**, *139*, 4250.

# *Outline*

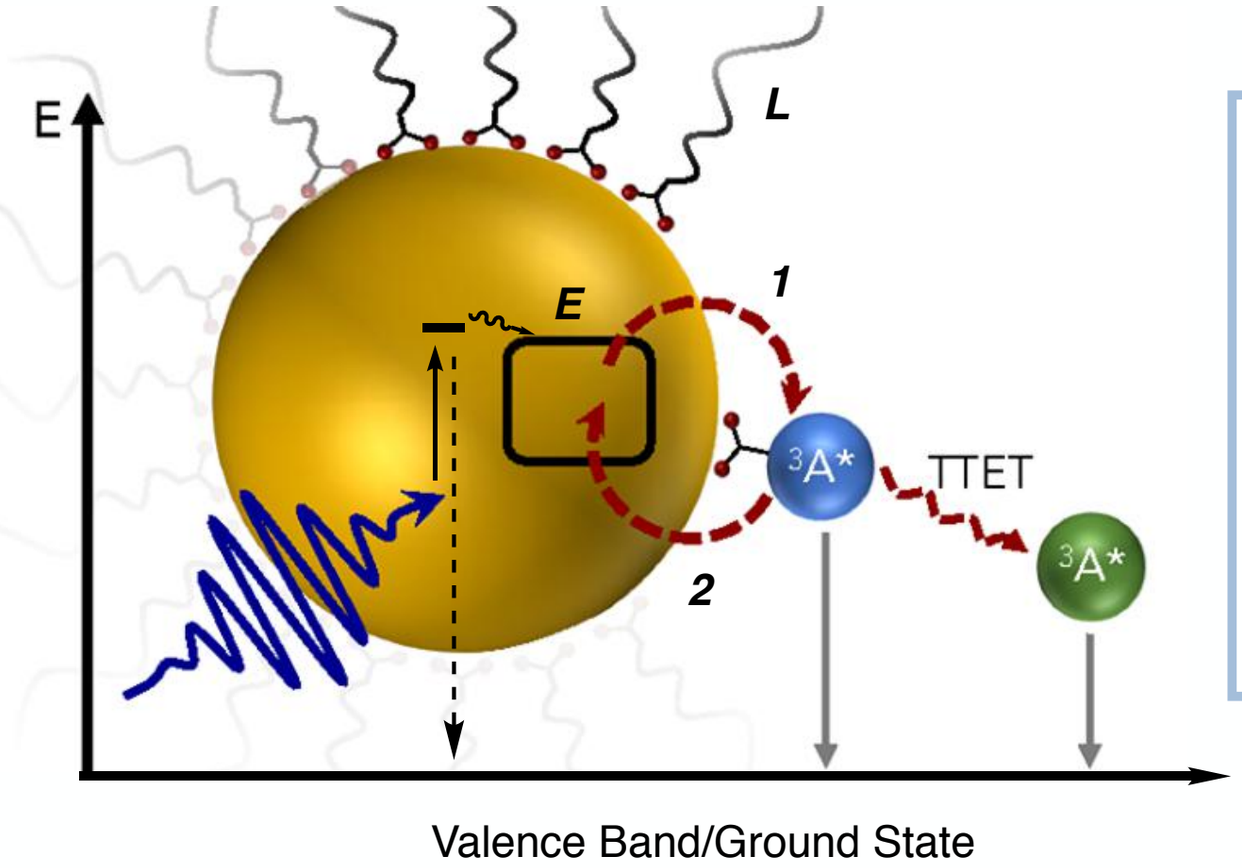
- *Background*
  - quantum confinement
  - tunable optical properties
  - tunable electronic properties

- *Applications in electron transfer processes*
  - general mechanistic scheme
  - net reductive and oxidative reactions
  - QDs as photocatalysts in photoredox reactions

- *Applications in energy transfer processes*
  - general mechanistic scheme
  - applications in photovoltaics
  - applications in biological systems



# *QDs in Energy Transfer Processes: General Mechanism*




**E**: triplet exciton

**L**: capping ligand on QD surface

**1**: triplet-triplet energy transfer (TTET)

**2**: reverse triplet-triplet energy transfer (rTTET)

$^3A^*$ : triplet energy acceptor on QD surface

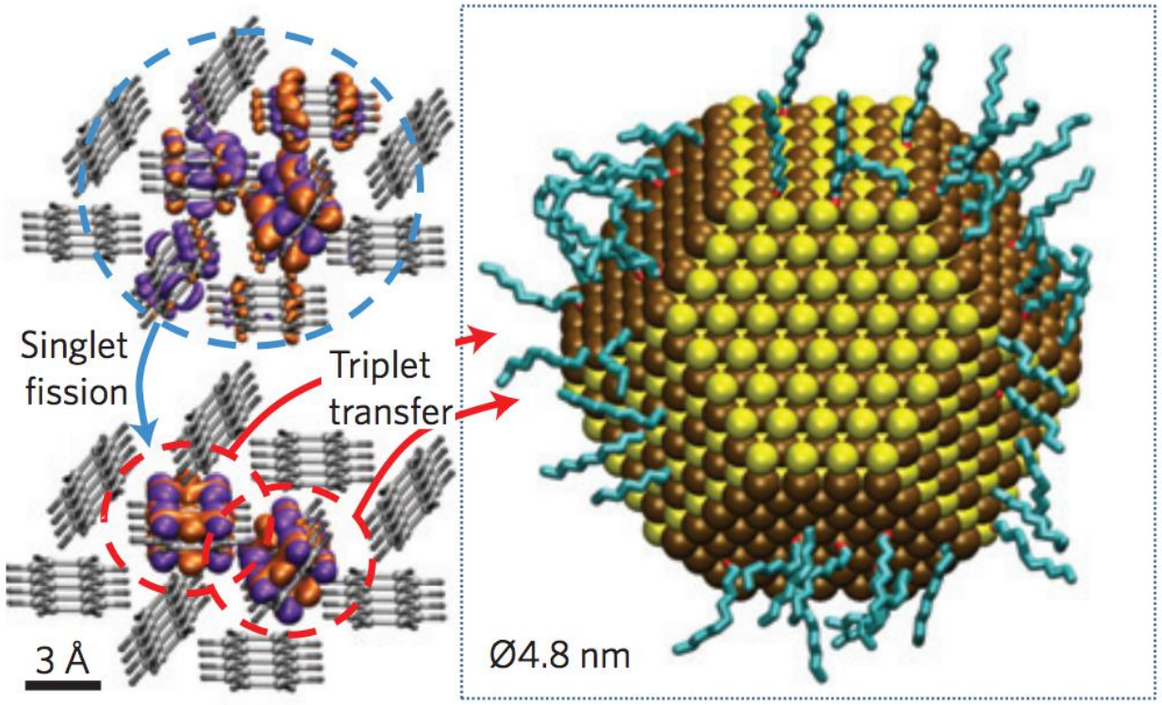
$^3A^*$ : triplet energy acceptor in solution

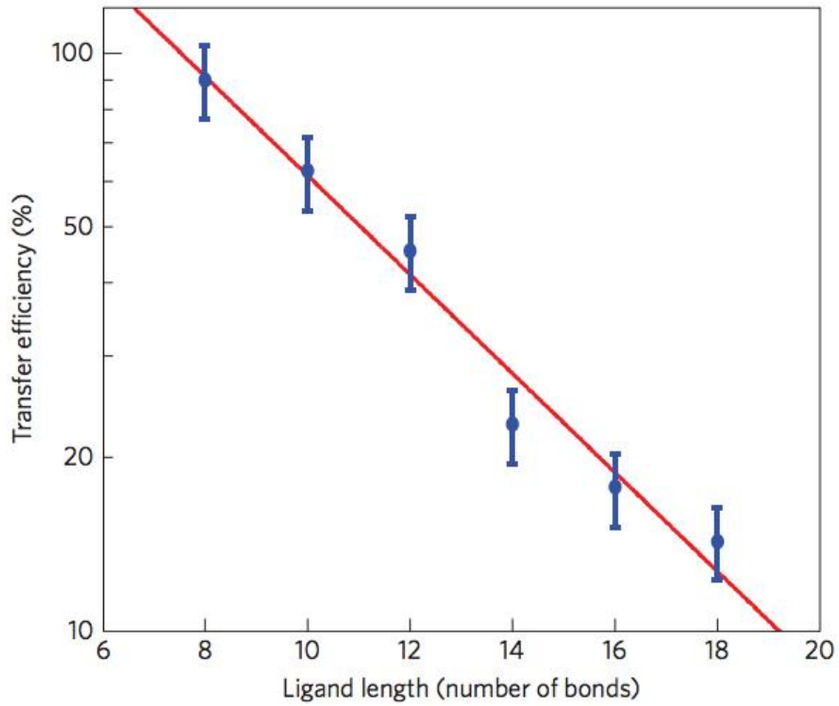
- *triplet energies tunable based on bandgap of QD material*
- *TTET competitive with excited-state decay to GS (~ $10^2$ ns)*

*Inorg. Chem.* **2018**, *57*, 2351.
*Science*, **2016**, *351*, 369.

# *QDs in Energy Transfer Processes: Early Applications*

- TTET from organic molecules to QDs at interface



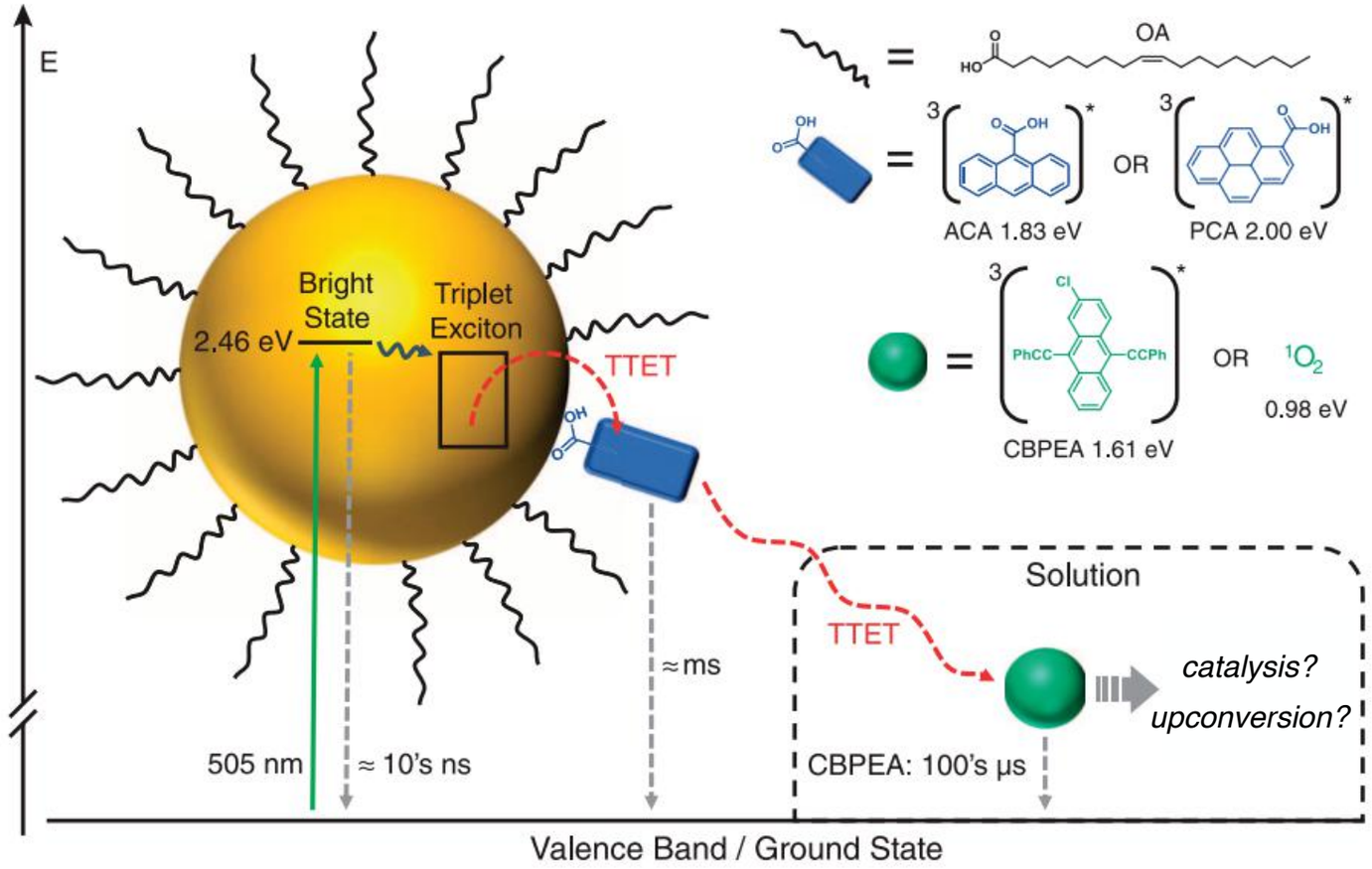

- *PbS as QD coated with tetracene*
- *similar study with pentacene and PbSe QDs*
- *tetracene triplets generated via singlet fission*
- *efficiency of EnT decrease as ligand length increase*
- *TTET only observed when QD bandgap ≈ triplet energy tetracene*

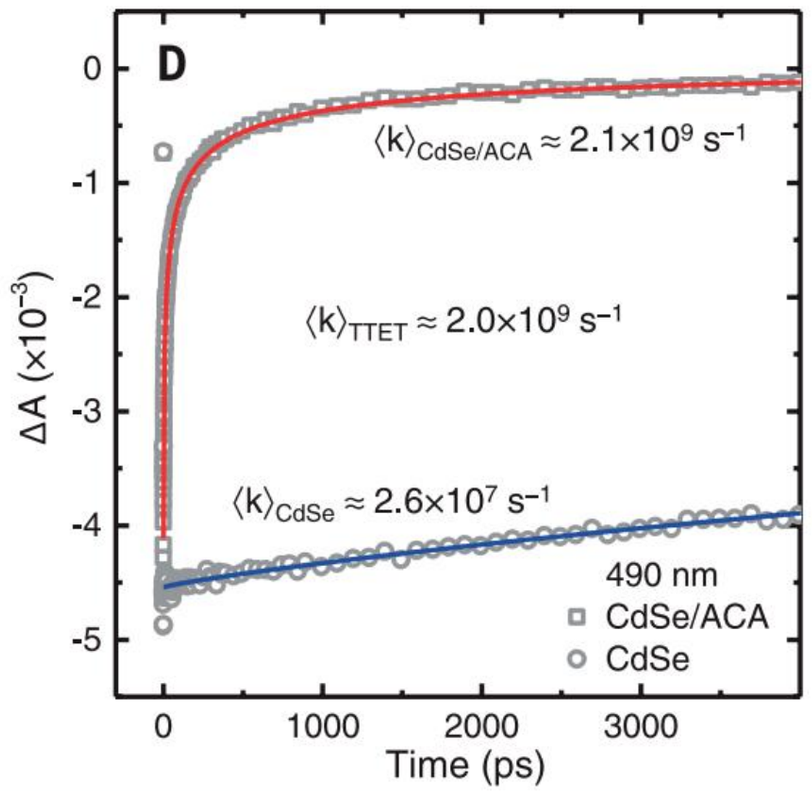

*Nat. Mater.* **2014**, *13*, 1033.

*Nat. Mater.* **2014**, *13*, 1039.

# *QDs in Energy Transfer Processes: Early Applications*

- First demonstration of TTET from QD to organic molecules at QD surface



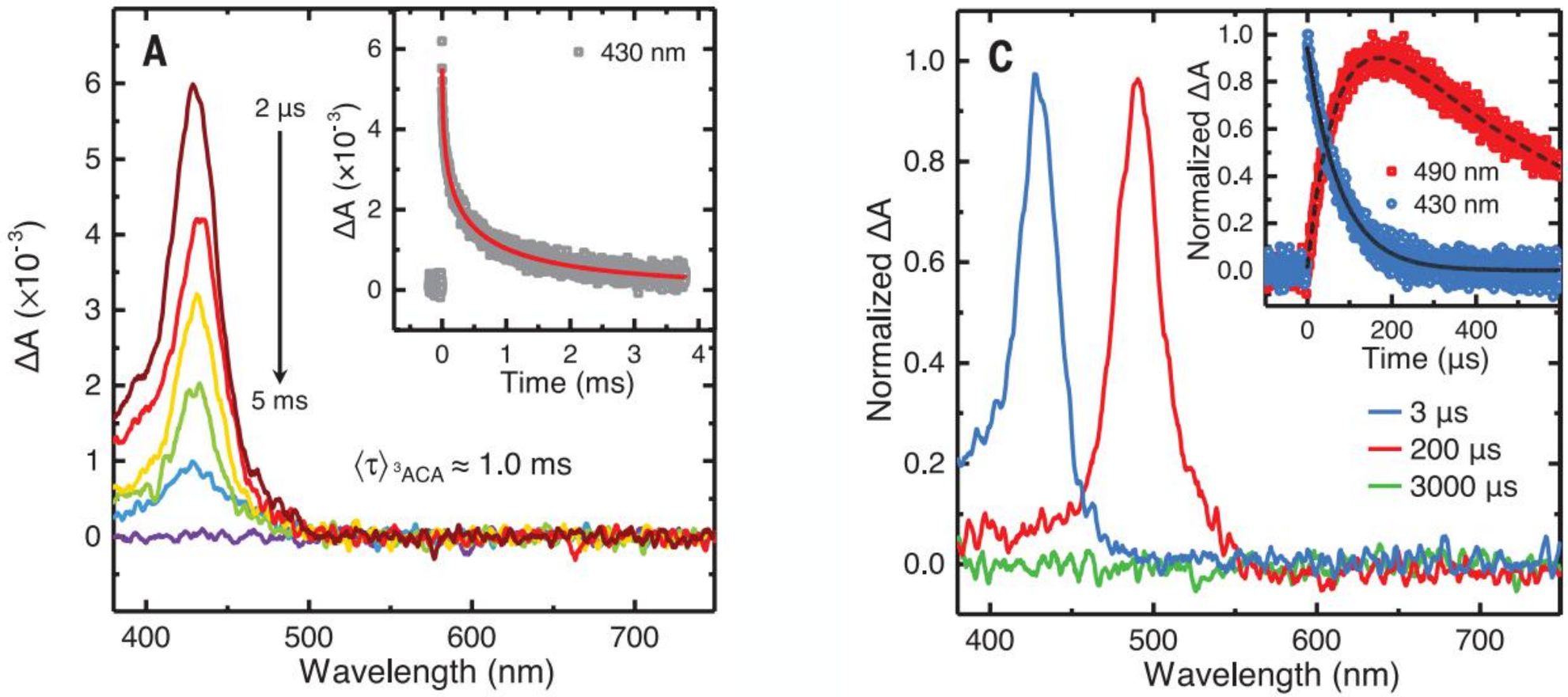

***no TTET from QD to anthracene or pyrene observed (though thermodynamically feasible)***

**carboxylate functionality was required for prior adsorption onto QD surface**

*Science*, **2016**, *351*, 369.

# *QDs in Energy Transfer Processes: Early Applications*

- First demonstration of TTET from QD to organic molecules at QD surface




***lifetime of surface-anchored organic molecules ~ ms timescale***

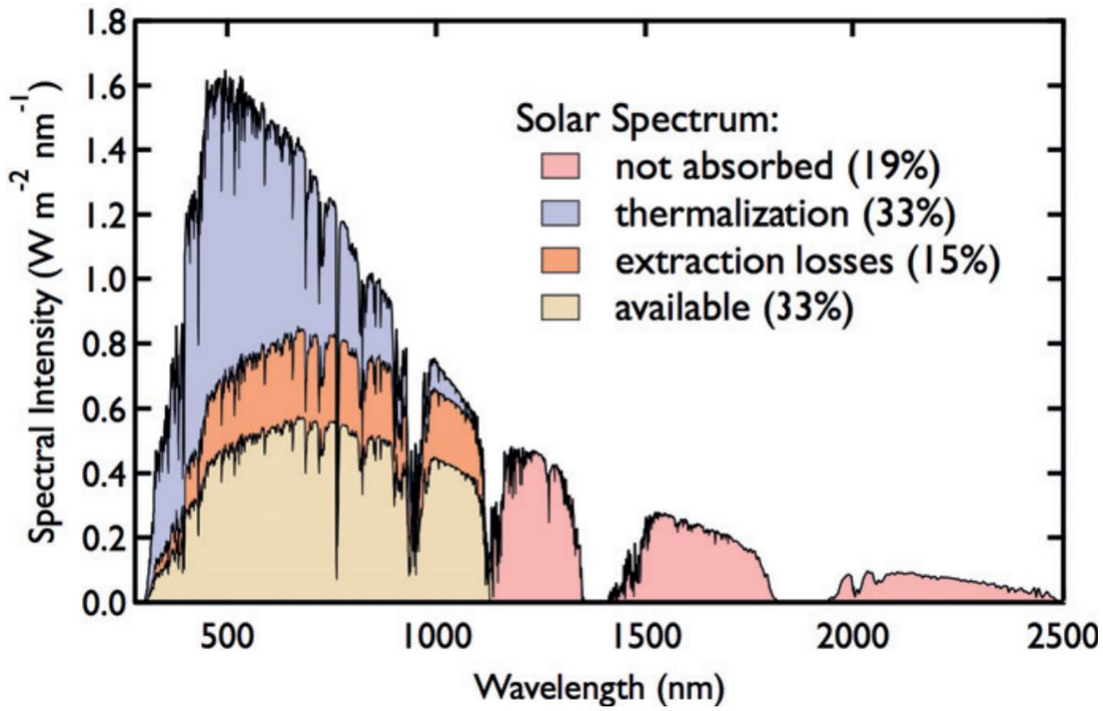
***TTET was observed between $^3$ACA$^*$ and CBPEA present in solution ~ ns timescale***

***demonstrated that triplet excitons from QD can be transfered to bulk solution***

*Science*, **2016**, *351*, 369.

# *QDs in Energy Transfer Processes: Application in Photovoltaics*

*energetic losses for typical Si solar cell ($E_g$ = 1.1 eV)*




***can quantum dots be used to overcome the Shockley-Quessier limit?***

***possible strategy: photon upconversion***


*Materials Today*, **2012**, *15*, 508.

*Nat. Phot.* **2016**, *10*, 31.

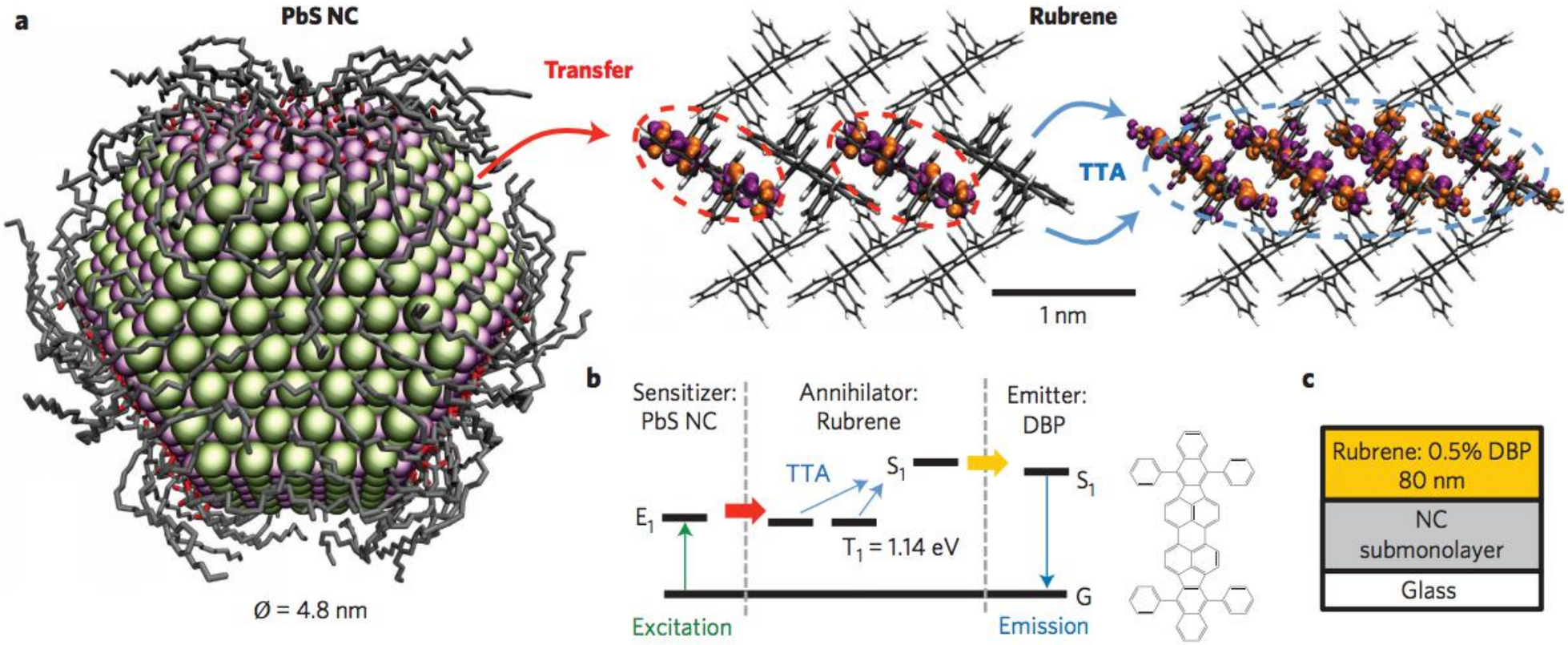
# *QDs in Energy Transfer Processes: Photon Upconversion*

- *infrared-to-visible photon upconversioin using PbS QDs*

*Nat. Phot.* **2016**, *10*, 31.

# *QDs in Energy Transfer Processes: Photon Upconversion*

- infrared-to-visible photon upconversioin using PbS QDs



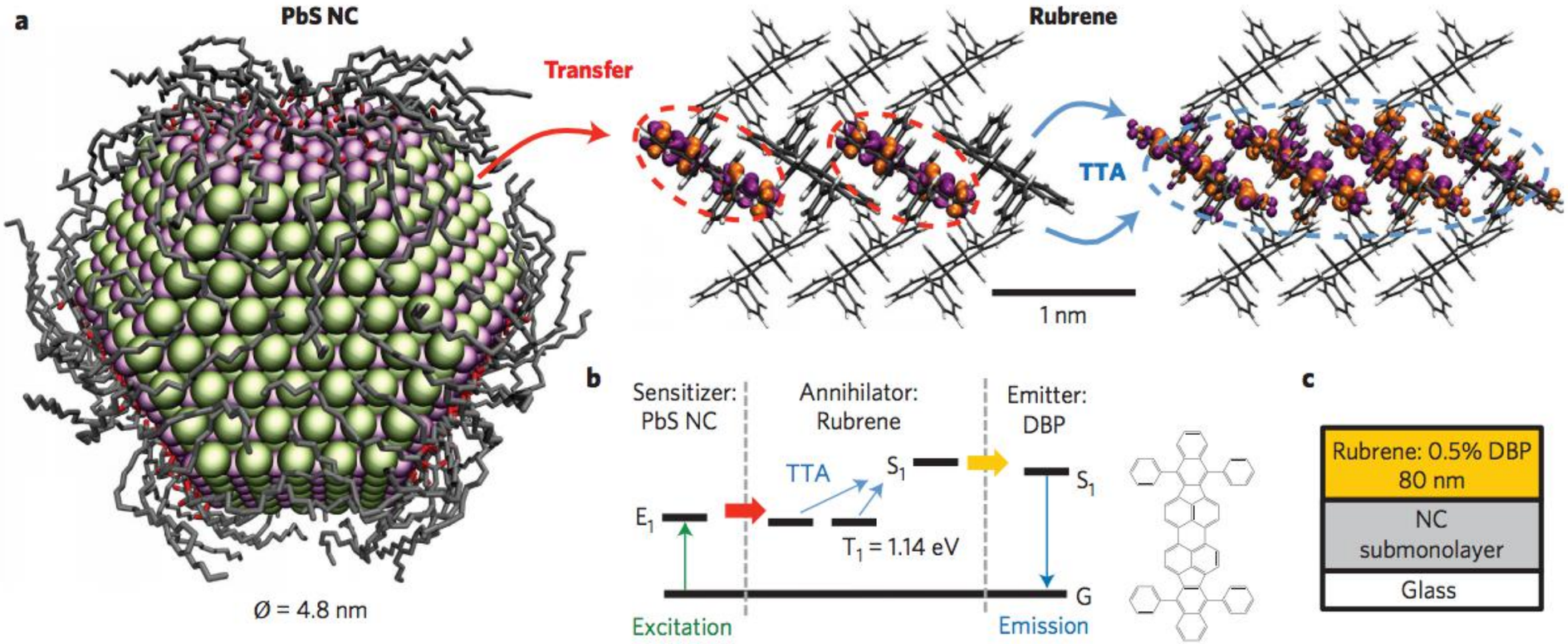

***TTET to rubrene molecules, which undergo TTA and subsequent energy transfer to emitter***

***λ = 808 nm excitation of PbS QDs led to an upconversion up to λ = 612 nm***

*Nat. Phot.* **2016**, *10*, 31.

# *QDs in Energy Transfer Processes: Photon Upconversion*

- infrared-to-visible photon upconversioin using PbS QDs



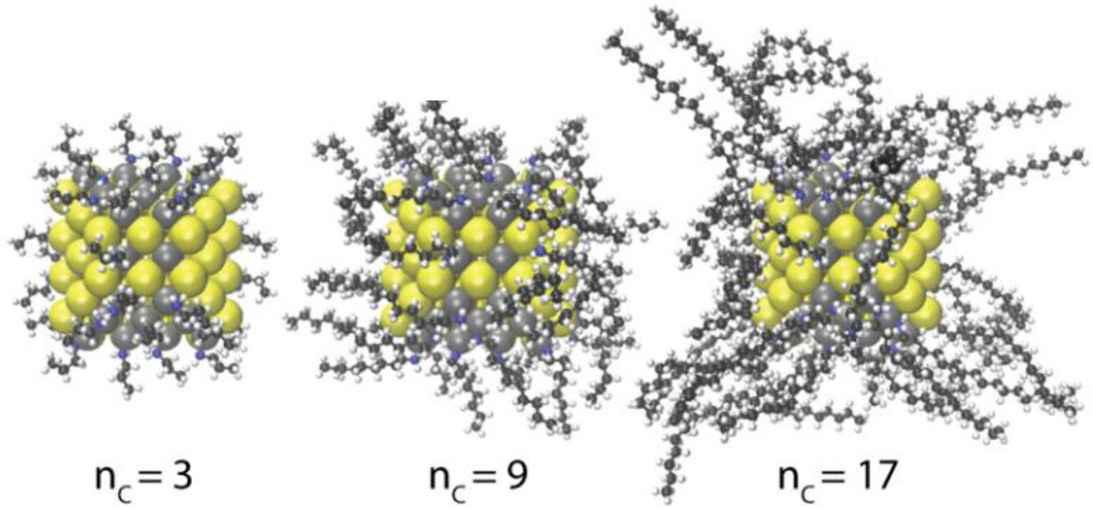

***measured upconversion quantum efficiency at varying PbS QD size:***

$\eta_{(850\ nm)} = (1.2 \pm 0.2)\%$, $\eta_{(960\ nm)} = (0.51 \pm 0.07)\%$, $\eta_{(1{,}010\ nm)} = (0.21 \pm 0.03)\%$

*Nat. Phot.* **2016**, *10*, 31.

# *QDs in Energy Transfer Processes: Photon Upconversion*

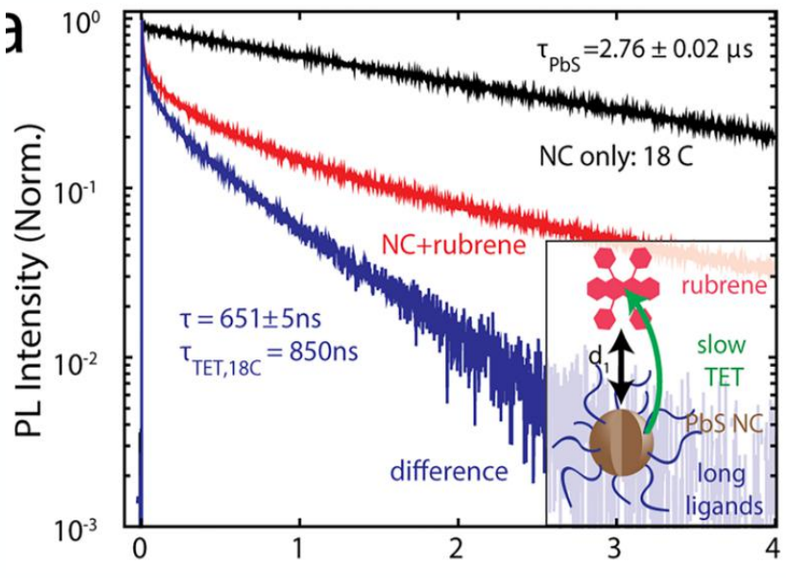
- Further tuning of PbS - rubrene system by altering ligand size

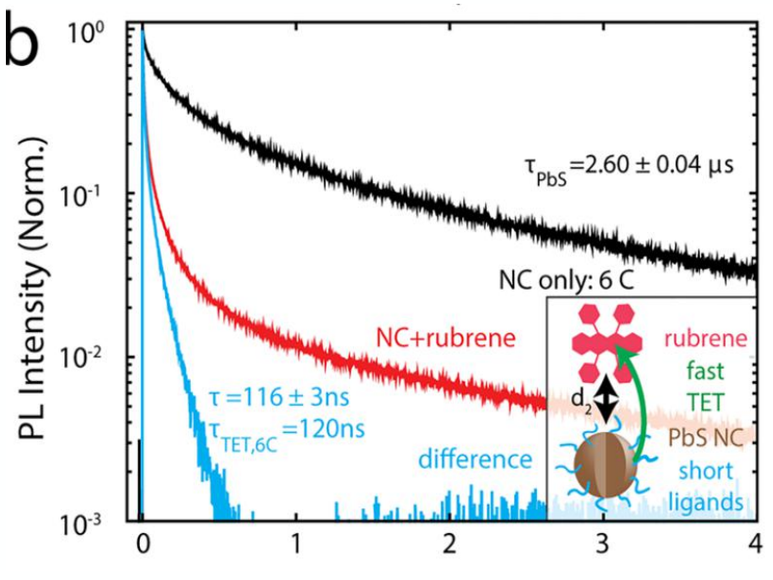



*decreasing length of capping ligand*

*from 18 to 6 carbon units*

*led to increased TTET rates*

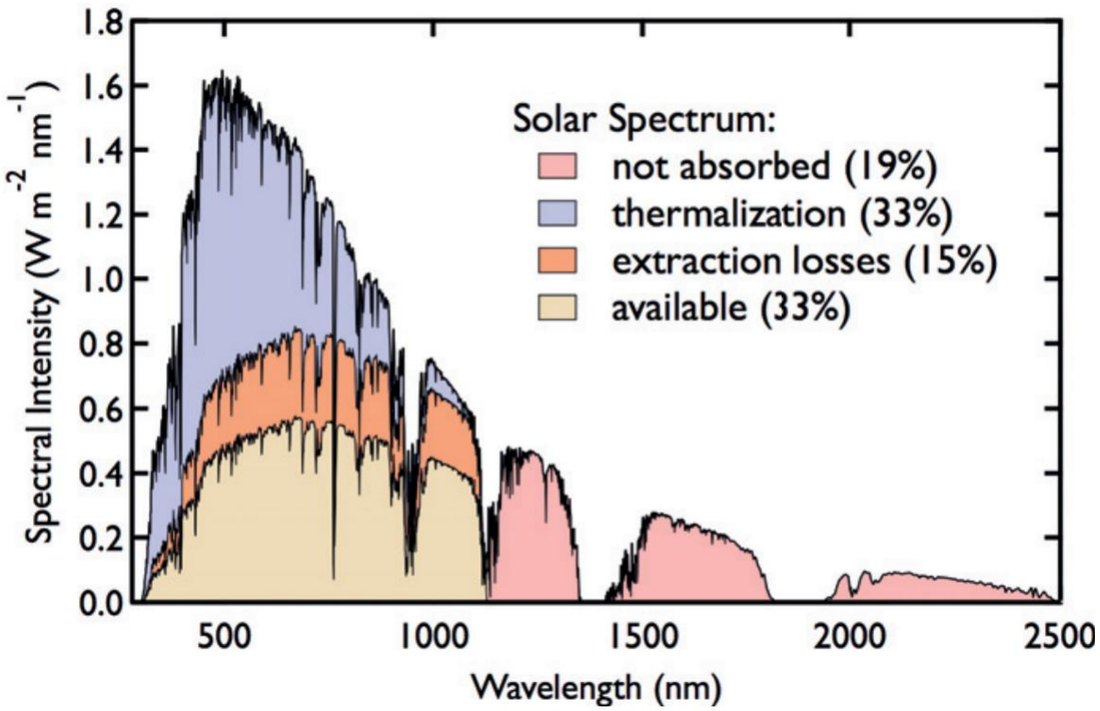



*ACS Nano.* **2017**, *11*, 7848.

# *QDs in Energy Transfer Processes: Application in Photovoltaics*

*energetic losses for typical Si solar cell ($E_g$ = 1.1 eV)*




***can quantum dots be used to overcome the Shockley-Quessier limit?***

***possible strategy: carrier multiplication***

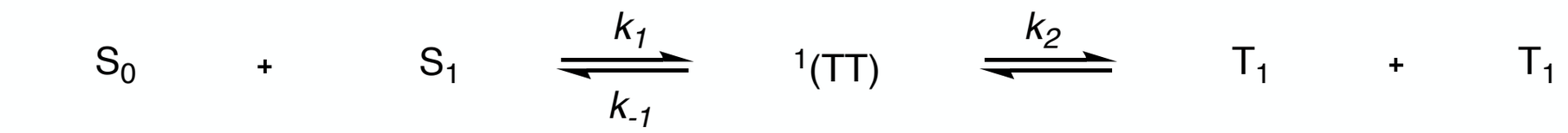

*Materials Today*, **2012**, *15*, 508.

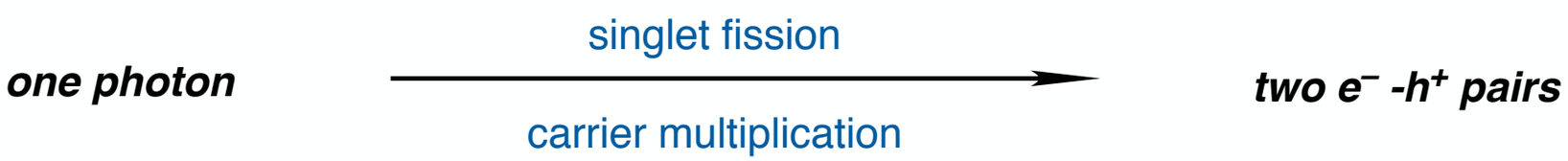
*Nat. Phot.* **2016**, *10*, 31.

# *QDs in Energy Transfer Processes: Carrier Multiplication*

- Using singlet fission molecules as ligands for carrier multiplication

**singlet fission**



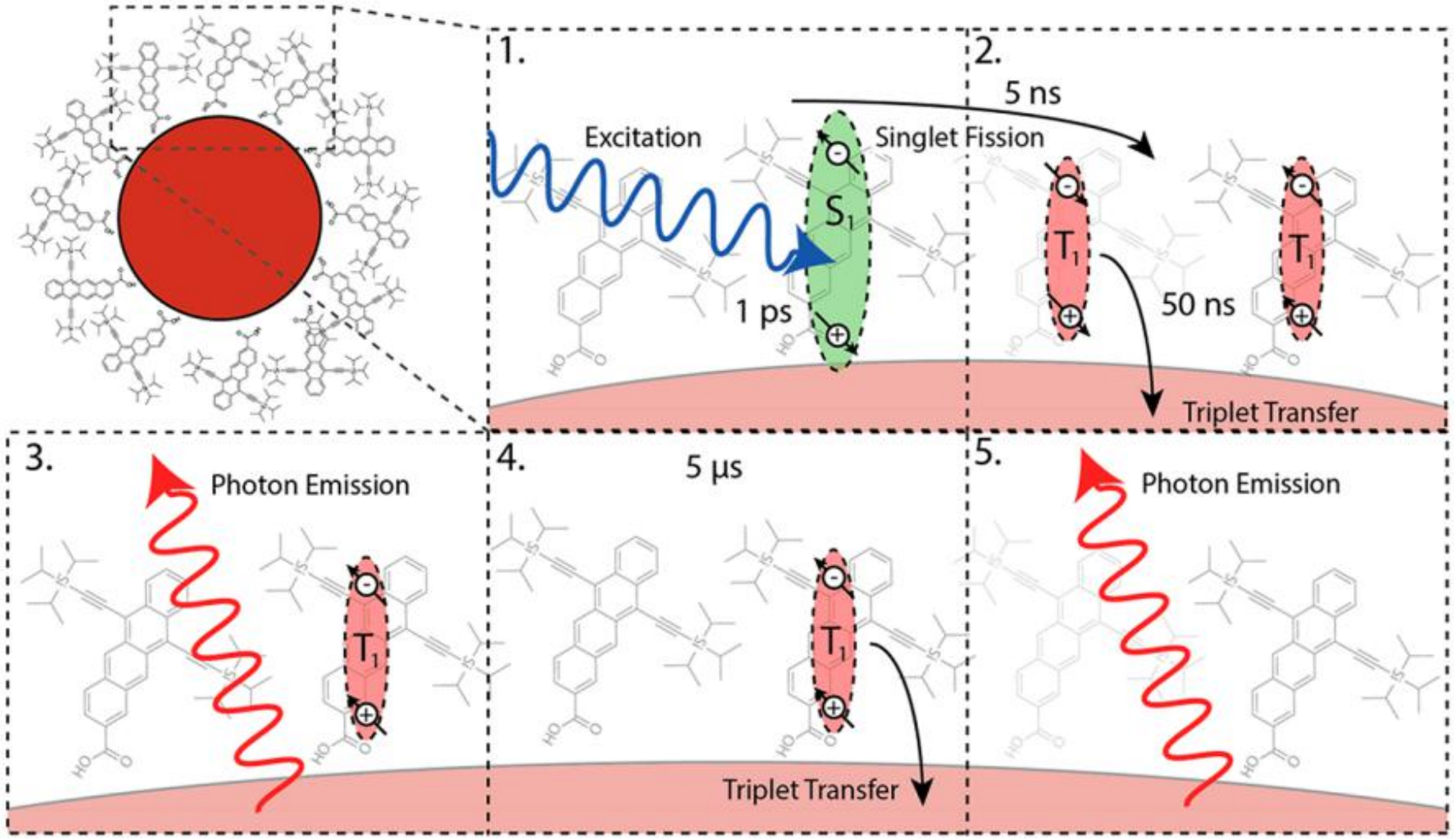




- high energy photon converted to two low-energy $e^-$ -$h^+$ pairs
- can be absorbed by low-bandgap materials, reducing thermalization losses

*J. Phys. Chem. Lett.* **2018**, *9*, 1454.

# *QDs in Energy Transfer Processes: Carrier Multiplication*

- Using singlet fission molecules as ligands for carrier multiplication: design strategy



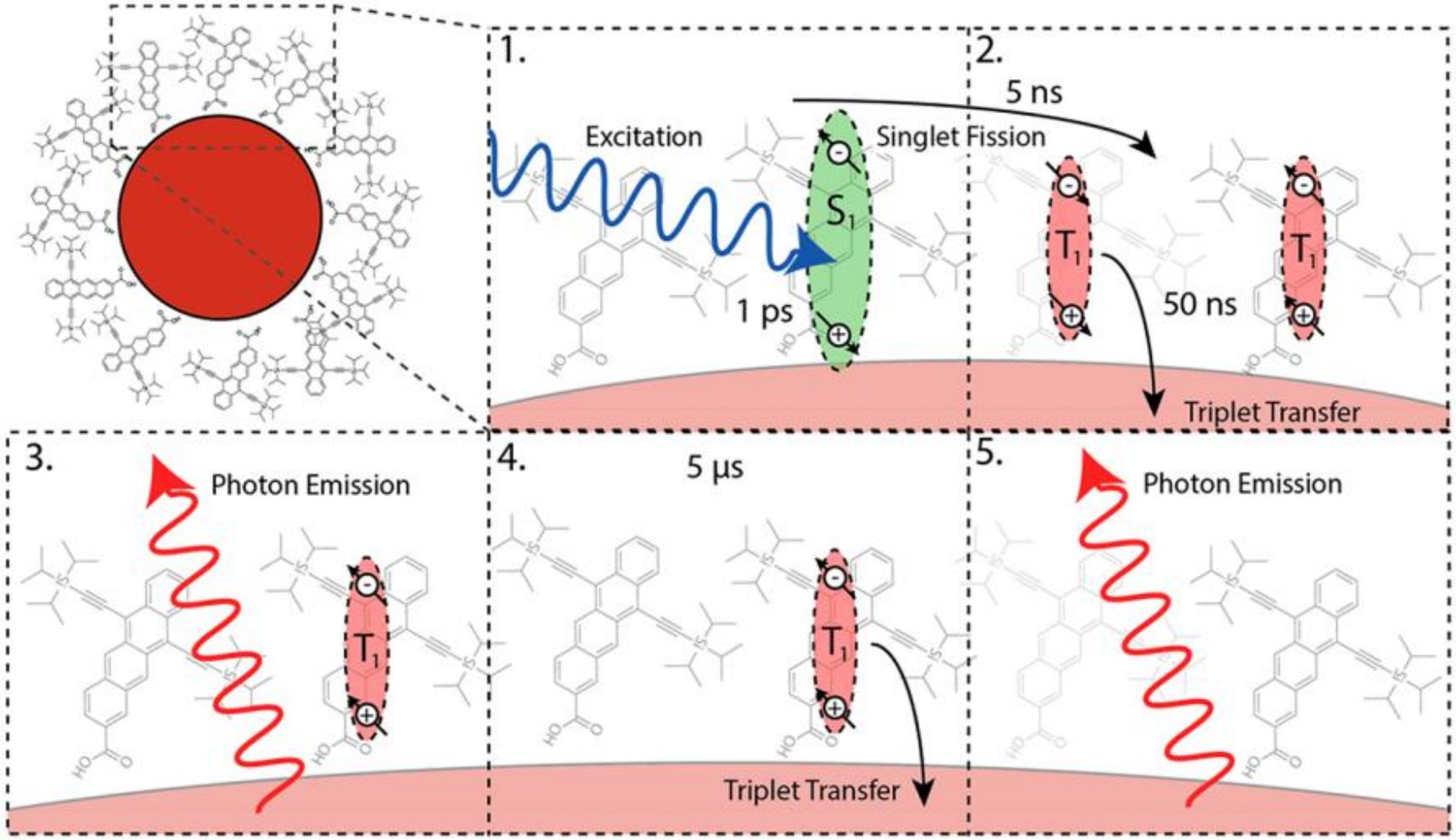

*requires two **sequential** triplet transfer steps to QD*

*using TIPS-tetracene carboxylic acid as singlet fission capping ligand*

*J. Phys. Chem. Lett.* **2018**, *9*, 1454.

# *QDs in Energy Transfer Processes: Carrier Multiplication*

- Using singlet fission molecules as ligands for carrier multiplication



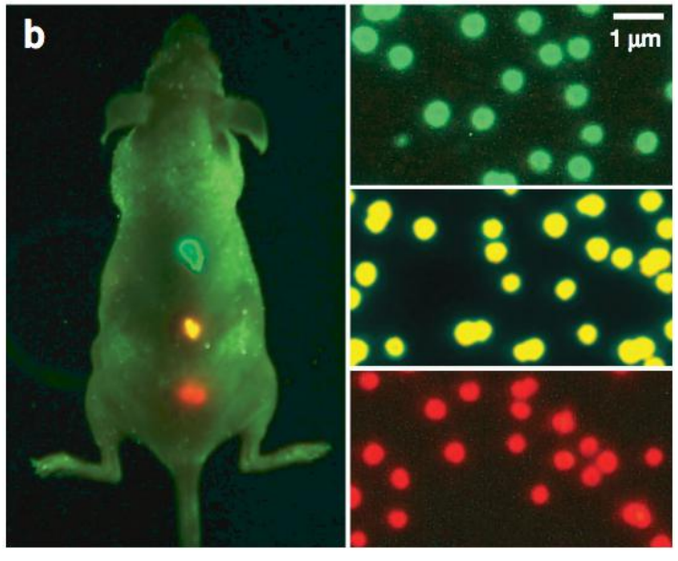

*no delayed photoluminescence (indicative of TTA) observed*

*observe doubling of photoluminescence quantum efficiency using SF ligands*

*further studies required to understand mechanism*

*J. Phys. Chem. Lett.* **2018**, *9*, 1454.

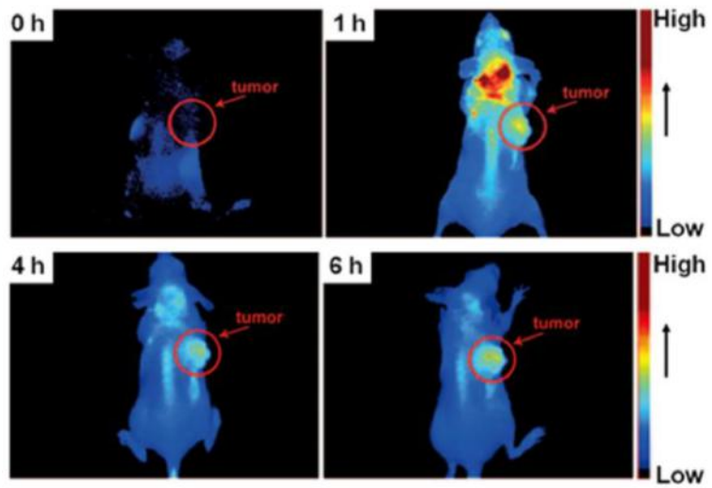
# *Quantum Dots: Biological Applications*




***in vivo bioimaging***

***smartphones and custom bioanalytic devices***

***drug delivery and cancer therapy***




***near IR QDs for deep tissue imaging***

*Chem. Rev.* **2015**, *115*, 11669.

# *QDs in Energy Transfer Processes: Quntum Dot Bioconjugates*

- Moving from hydrophobic capping ligands to biocompatible QDs

***requirements for biocompatible QD ligands***

- affinity for QD surface
- stability in various pHs
- minimal toxicity
- can be further conjugated with biomolecules
- minimal nonspecific binding in biological systems

- QD and energy transfer in biological systems

***Förster Resonance Energy Transfer (FRET)***

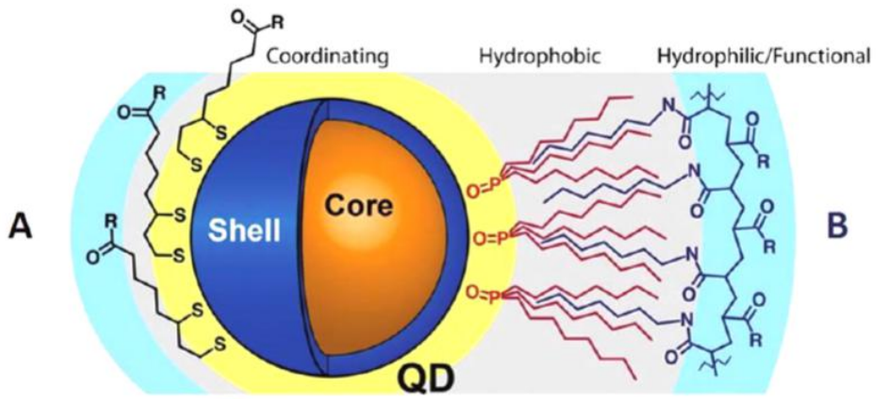
energy transfer from excited state donor to acceptor through long-range dipole-dipole coupling

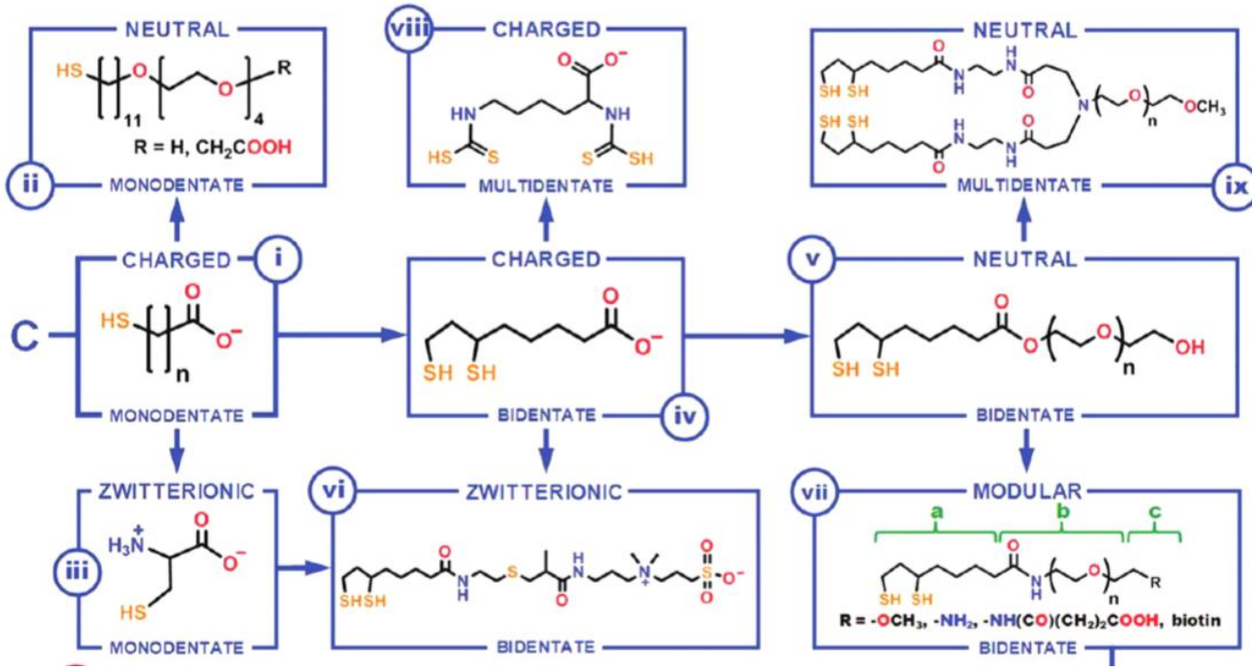
*"long-range" typically <10 nm, comparable scale to QD and biomolecular conjugate*

For review on EnT and QD Bioconjugates, see: *Chem. Rev.* **2017**, *117*, 536.

# *QDs in Energy Transfer Processes: Quntum Dot Bioconjugates*

- Methods for synthesis of biocompatible QDs from presynthesized QDs




**A:** ligand exchange to water-soluble anchoring ligands

**B:** hydrophilic group appended onto hydrophobic caps

***challenges***

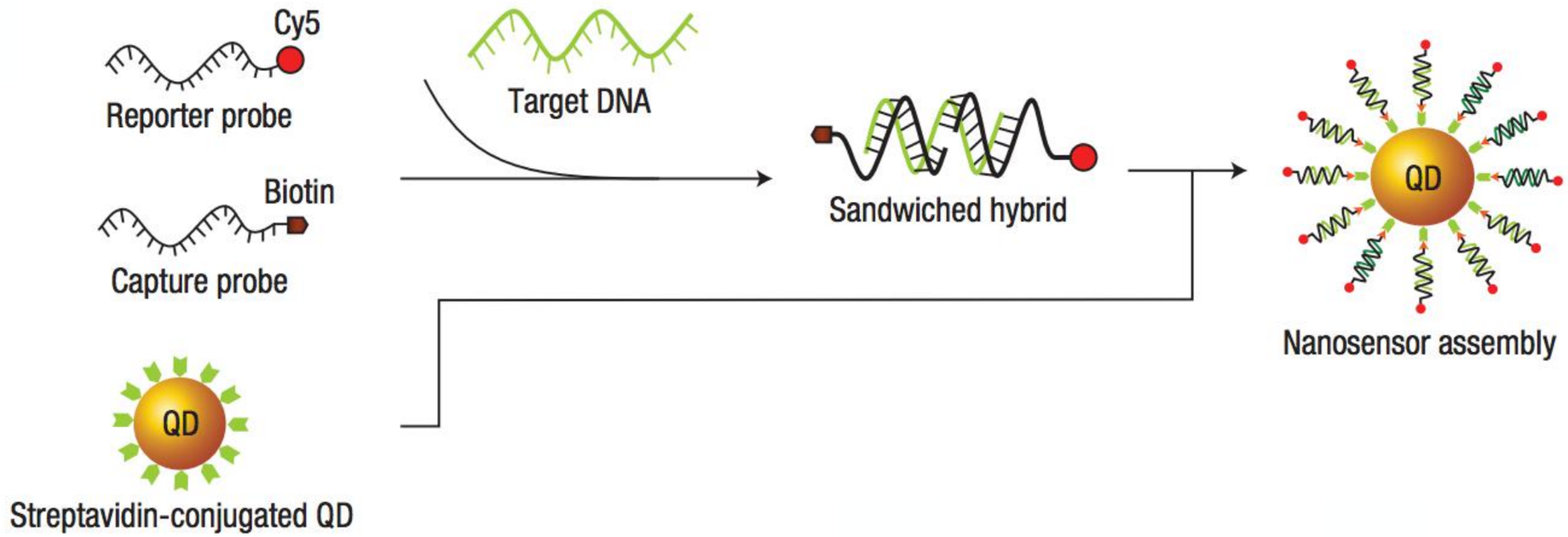
- maintaining water solubility at varying pH
- maintaining surface anchoring at varying pH

**multidentate ligands C viii and ix showed long term colloidal stability over range of pHs**

For review on EnT and QD Bioconjugates, see: *Chem. Rev.* **2017**, *117*, 536.

# *QDs in Energy Transfer Processes: FRET probes*

- QDs as ultrasensitive nanosensors for detection of DNA point mutation



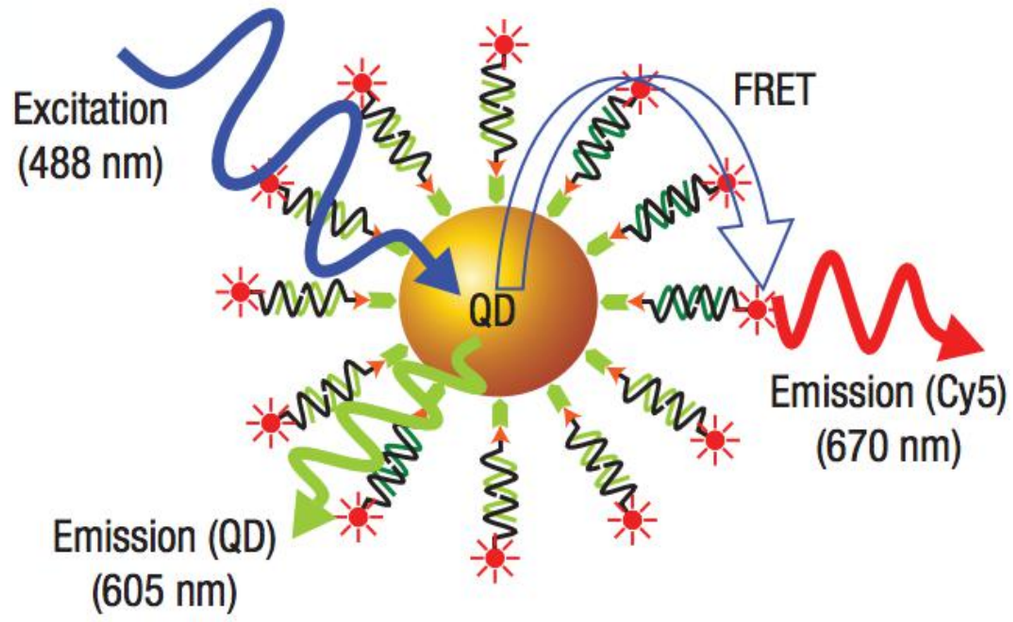

***quantum dot serves as both FRET energy donor and target concentrator***

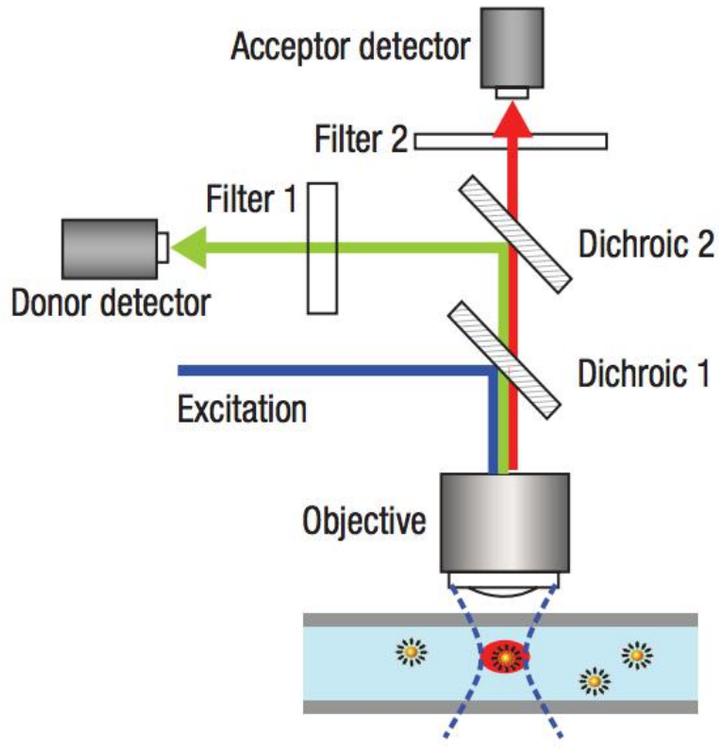
***several targets captured by single QD through biotin-streptavidin binding***

*Nature Materials* **2005**, *4*, 826.

# *QDs in Energy Transfer Processes: FRET probes*

- QDs as ultrasensitive nanosensors for detection of DNA point mutation



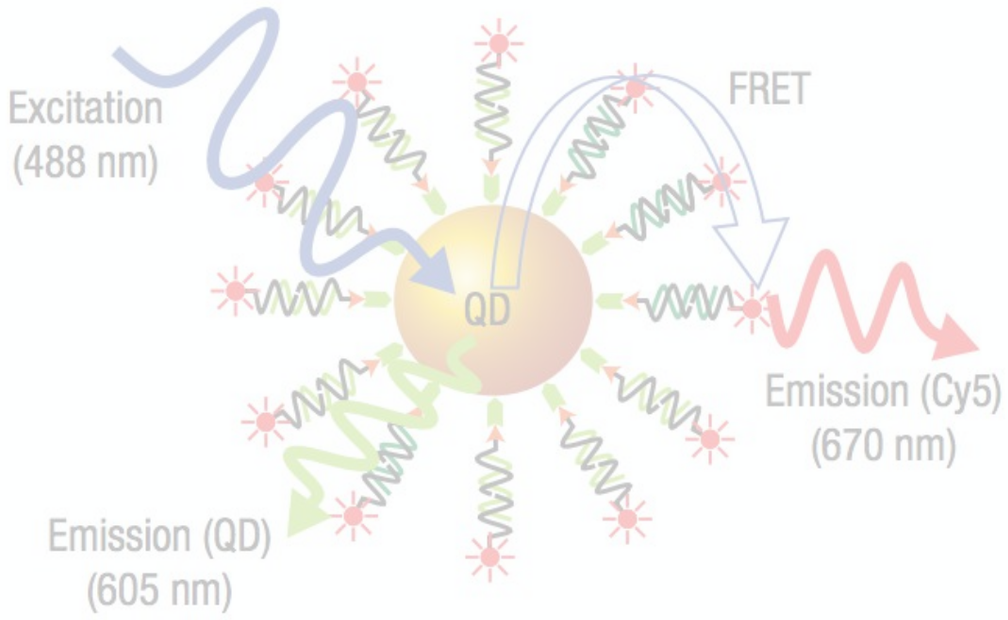

***different emission of QD and fluorscent probe after FRET***

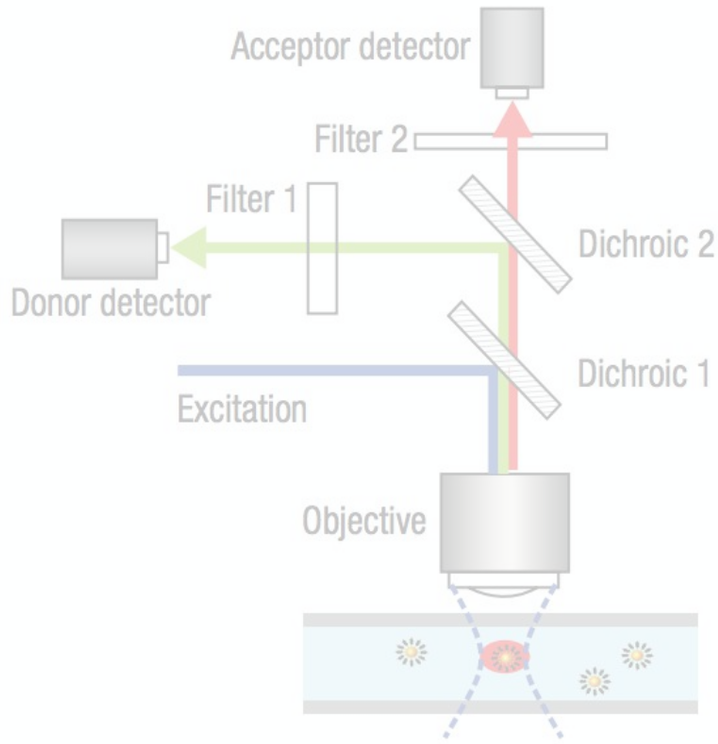
***experimental setup allows for detection of FRET emission signals with no background***

*Nature Materials* **2005**, *4*, 826.

# *QDs in Energy Transfer Processes: FRET probes*

- QDs as ultrasensitive nanosensors for detection of DNA point mutation

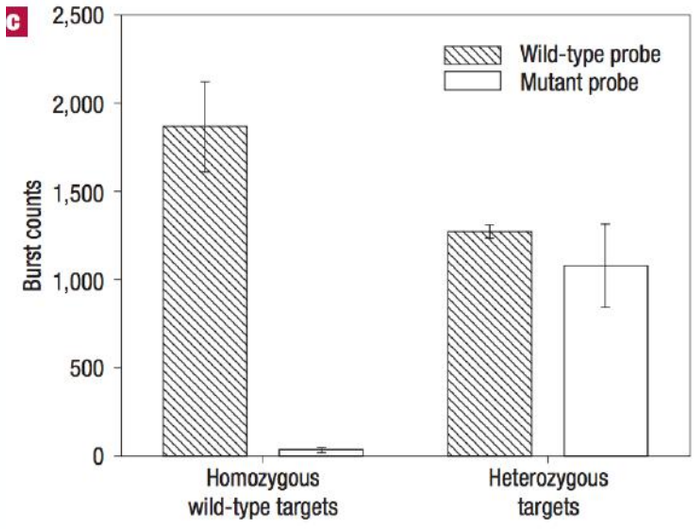



clinical samples from patients with ovarian tumors (SBTs)

pre-ligation step – only Kras mutation point are captured by probes

successful detection of point mutation typical of some ovarian tumors




*Nature Materials* **2005**, *4*, 826.

*Questions?*