

Nanoscience galore: *hybrid and nanoscale photonics*

Pavlos Lagoudakis

SOLAB, 11 June 2013

Hybrid nanophotonics

Nanostructures:
light harvesting and light emitting devices

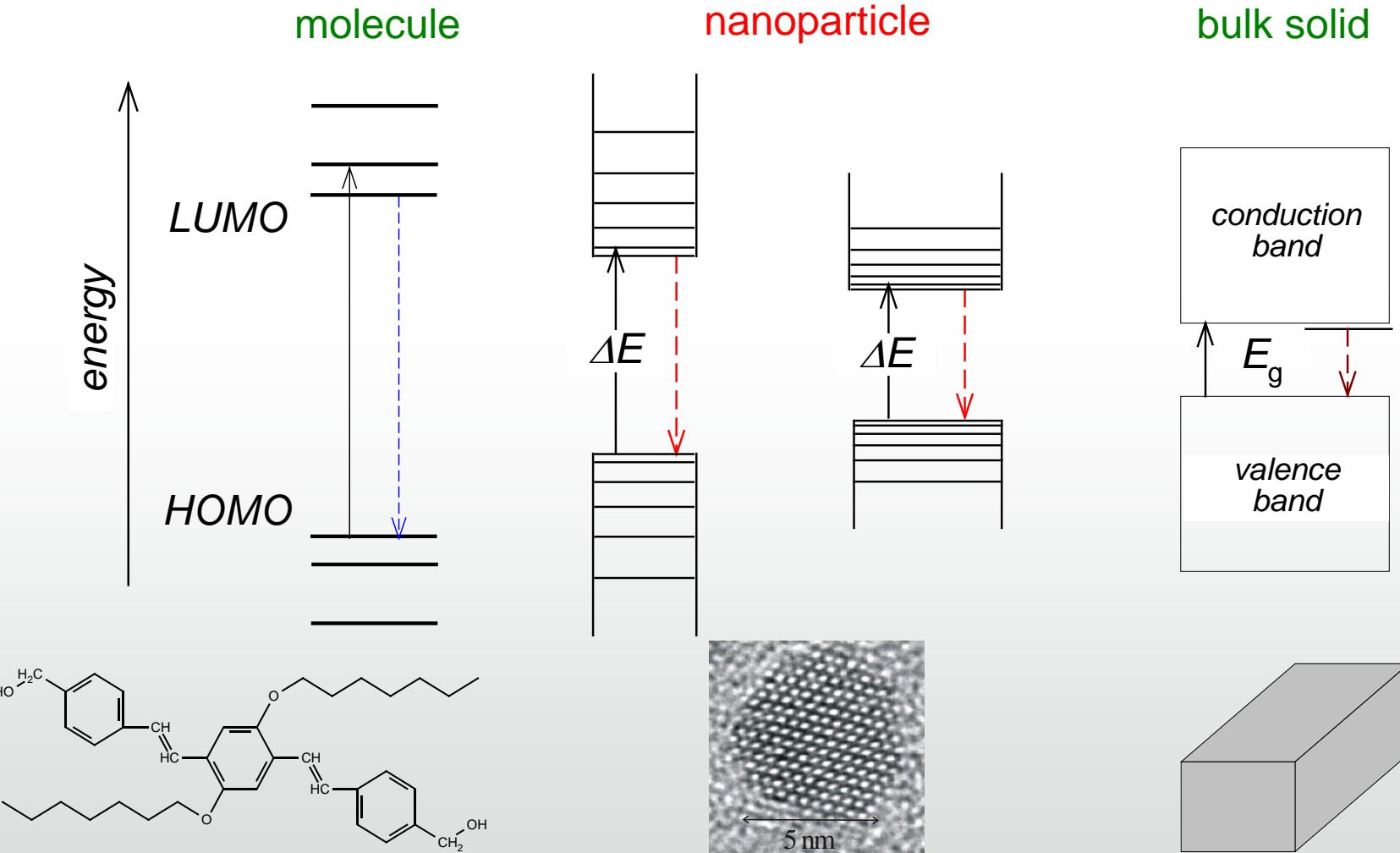
Hybrid nanophotonics

Nanostructures:
light harvesting and light emitting devices

Hybrid semiconductor materials:

- . epitaxial heterostructures/bulk crystals
- . colloidal QDs and/or organic semiconductors

Bulk, organic and colloidal nanocrystal semiconductor materials



Utilise best of both worlds

Colloidal QDs/organic

- High absorption
- Color tunability
- High quantum yield
- Low cost

Low carrier mobility

Epitaxial Semiconductors

High carrier mobility

Hybrid nanophotonics

Nanostructures:
light harvesting and light emitting devices

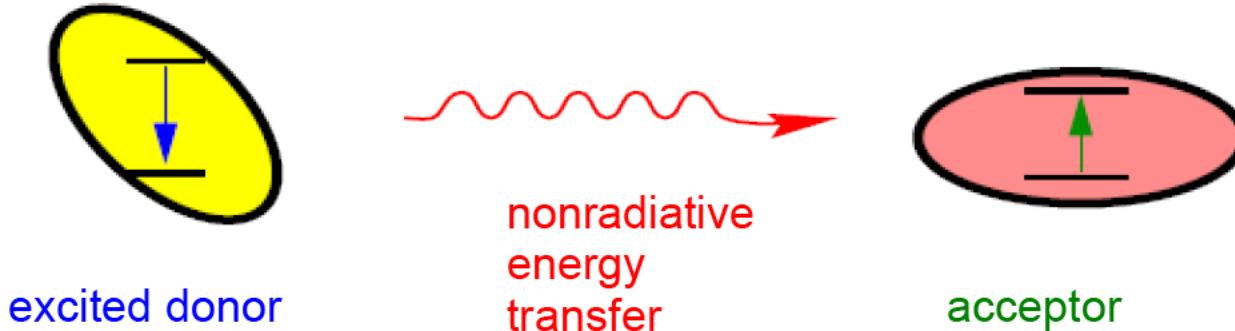
Hybrid semiconductor materials:

- . epitaxial heterostructures/bulk crystals
- . colloidal QDs and/or organic semiconductors

Energy transfer between constituents:

- . radiative pumping
- . non-radiative dipole-dipole coupling (RET)

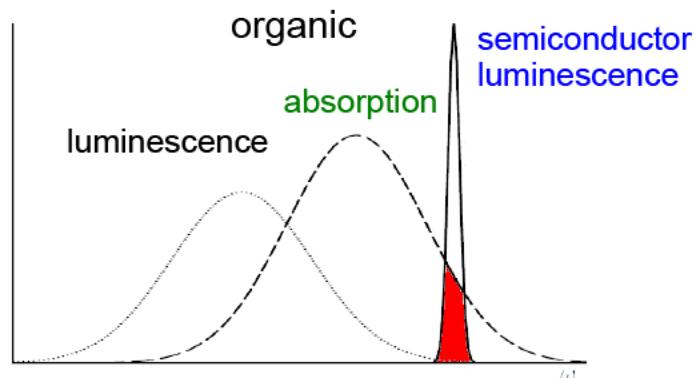
Resonance Energy Transfer



dipole - dipole interaction + Fermi golden rule \rightarrow

the energy transfer rate :

$$\frac{1}{\tau} \propto \frac{1}{R^6} \int \mathcal{L}(\omega) \mathcal{A}(\omega) \frac{d\omega}{\omega^4}$$

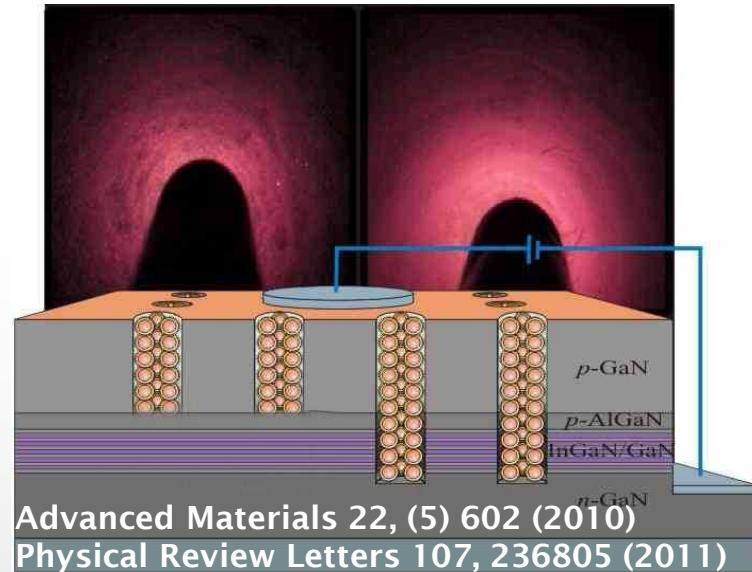
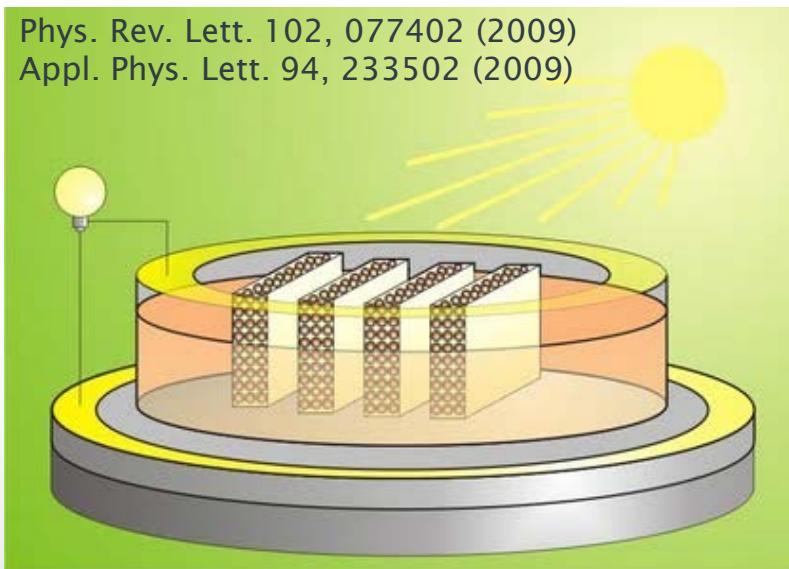


$\mathcal{L}(\omega)$ = donor
luminescence
spectrum

$\mathcal{A}(\omega)$ = acceptor
absorption
spectrum

Hybrid semiconductor nanostructures

Phys. Rev. Lett. 102, 077402 (2009)
Appl. Phys. Lett. 94, 233502 (2009)



- organic-inorganic, colloidal-epitaxial semiconductors
- weak coupling of electronic transitions

Hybrid Optoelectronics: Solar cells

- ▶ Efficient energy transfer in photosynthesis (rate $\propto R^{-6}$)
(Förster, Naturwissenschaften, 1948)
- ▶ Suggested for hybrid optoelectronics

(Dexter, Two ideas on energy transfer phenomena... , Journal of Luminescence, 1979,
extensive theoretical work by Agranovich & La Rocca)

D.L. Dexter; Two ideas on energy transfer phenomena

783

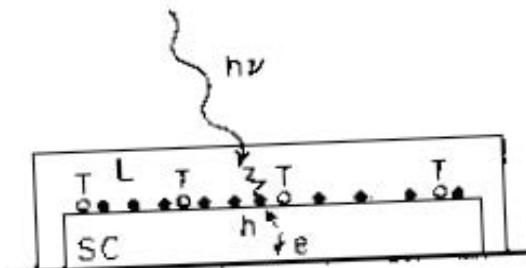
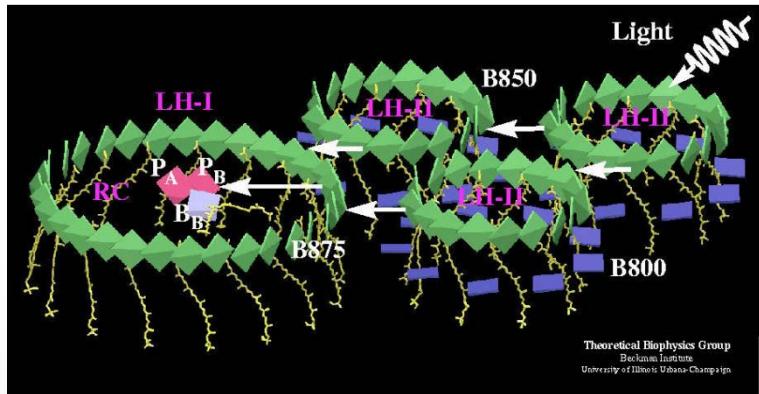


Fig. 2. Sketch of a photovoltaic cell consisting of a semiconductor SC and an organic layer L with some surface traps T. The solid circles denote a metallic grid of hole collectors.

- Chanyawadee et al., Photocurrent Enhancement in Hybrid Nanocrystal Quantum-Dot p-i-n Photovoltaic Devices, PRL (2009)
- Chanyawadee et al., Efficient light harvesting in hybrid CdTe nanocrystal/bulk GaAs p-i-n photovoltaic devices, APL (2009)
- Chanyawadee et al., Nonradiative exciton energy transfer in hybrid organic-inorganic heterostructures, PRB (2008)

Non-radiative energy transfer (RET)

Hu et al Quarterly reviews of biophysics 35, 1
(2002)



Energy transfer rate

\propto

overlap between donor emission
and acceptor absorption

\propto

R^{-n} *n=6 for point dipoles*
n=2 2D to 2D

H. Kuhn, J. Chem. Phys. **53**, 101 (1970).

Hybrid QW/nanophosphor LEDs

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School of Physics
and Astronomy

Eur. Phys. J. B 8, 353–362 (1999)

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Förster energy transfer from a semiconductor quantum well to an organic material overlayer

D. Basko^{1,a}, G.C. La Rocca^{1,b}, F. Bassani¹, and V.M. Agranovich²

¹ Scuola Normale Superiore and INFM, Piazza dei Cavalieri, 56126 Pisa, Italy

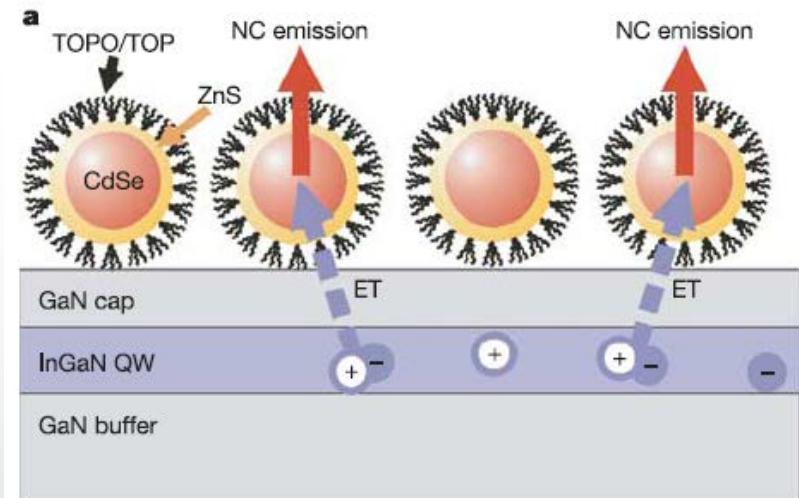
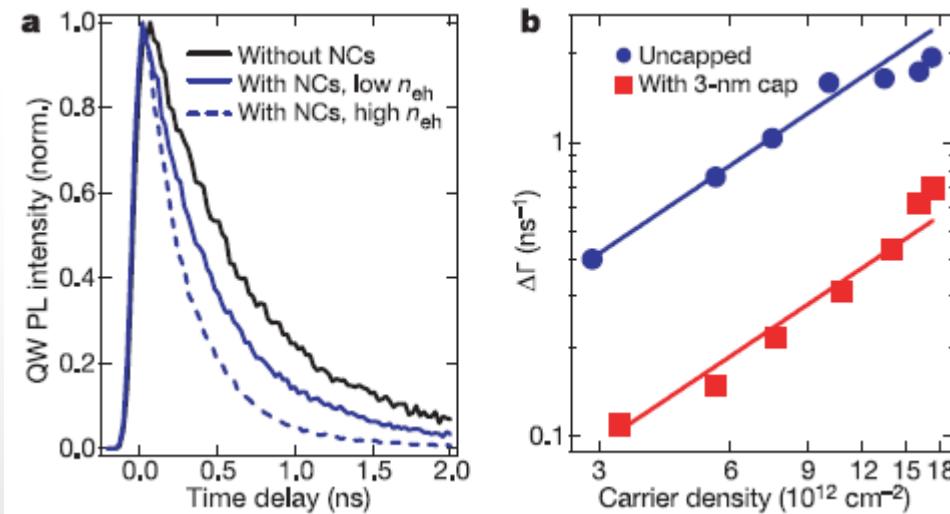
² Institute for Spectroscopy, Russian Academy of Sciences, Troitsk, Moscow region, 142092 Russia

Energy-transfer pumping of semiconductor nanocrystals using an epitaxial quantum well

Marc Achermann¹, Melissa A. Petruska¹, Simon Kos¹, Darryl L. Smith¹,
Daniel D. Koleske² & Victor I. Klimov¹

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²Sandia National Laboratories, Albuquerque, New Mexico 87185, USA



QW excitations: unbound electron hole pair regime

Förster energy transfer from a semiconductor quantum well to an organic material overlayer

D. Basko^{1,a}, G.C. La Rocca^{1,b}, F. Bassani¹, and V.M. Agranovich²

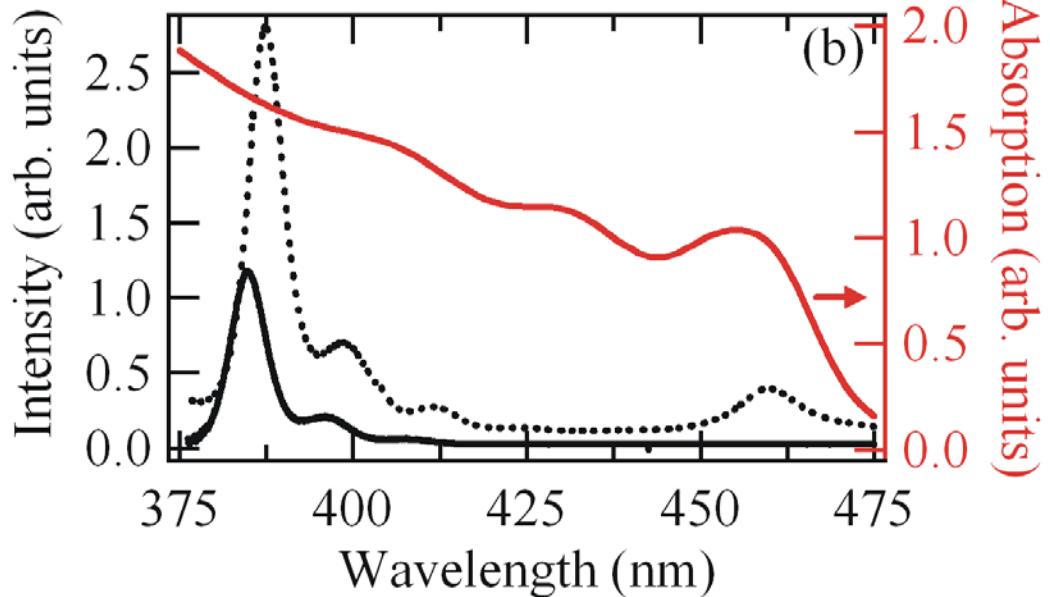
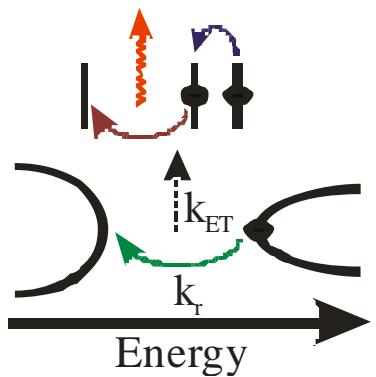
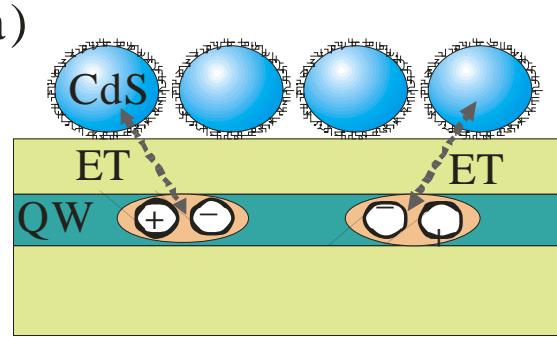
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² Institute for Spectroscopy, Russian Academy of Sciences, Troitsk, Moscow region, 142092 Russia

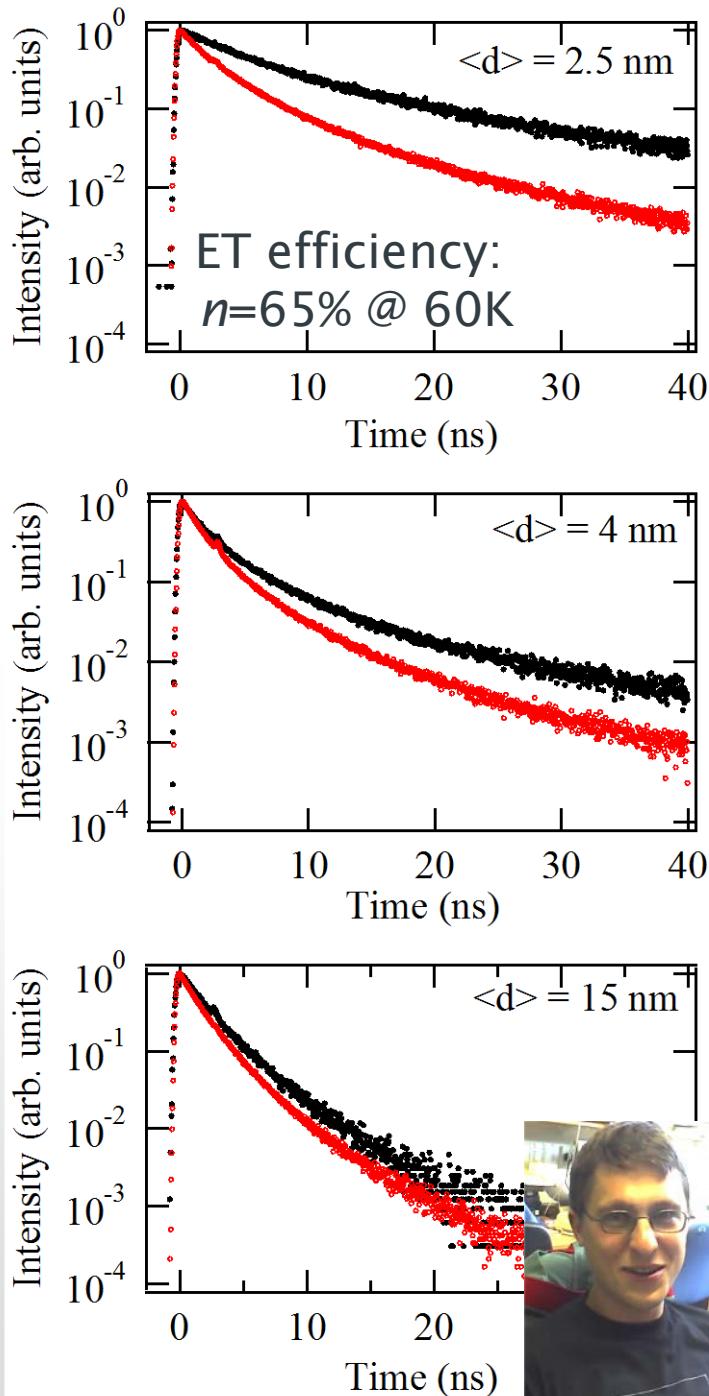
Abstract. We predict an efficient electronic energy transfer from an excited semiconductor quantum well to optically active organic molecules of the nearby medium (substrate and/or overlayer). The energy transfer mechanism is of the Förster type and, at semiconductor-organic distances of about 50 Å, can easily be as fast as 10–100 ps, which is about an order of magnitude shorter than the effective exciton lifetime in an isolated quantum well. In such conditions, the Wannier-Mott exciton luminescence is quenched and the organic luminescence is efficiently turned on. We consider both free as well as localized quantum well excitons discussing the dependence of the energy transfer rate on temperature and localization length. A similar mechanism for the non-radiative energy transfer to the organic overlayer molecules from unbound electron-hole pairs excited in the 2D continuum is shown to be much less competitive with respect to other relaxation channels inside the inorganic quantum well (in particular, 2D exciton formation).

Exciton Transfer in Hybrid Heterostructures

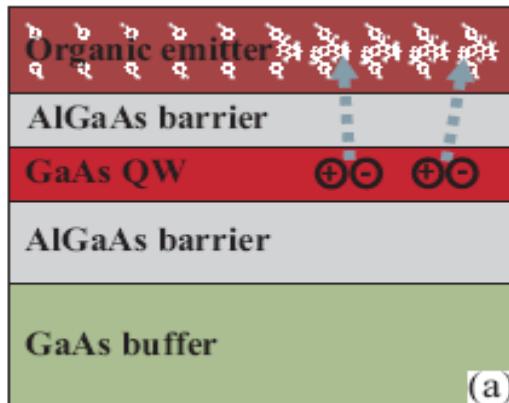
(a)



Rohrmoser et al Applied Physics Letters 2007

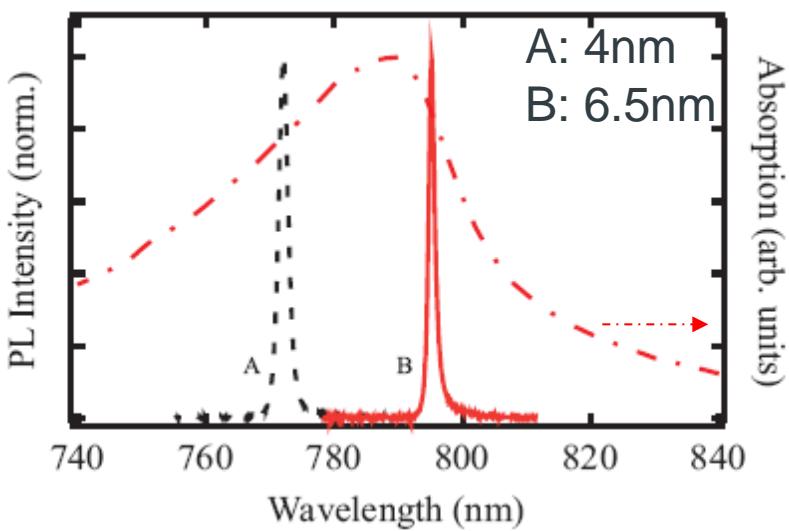


QW excitons to J-band excitons



Energy transfer rate:

$$k_{ET} = k_H - k_{QW}.$$

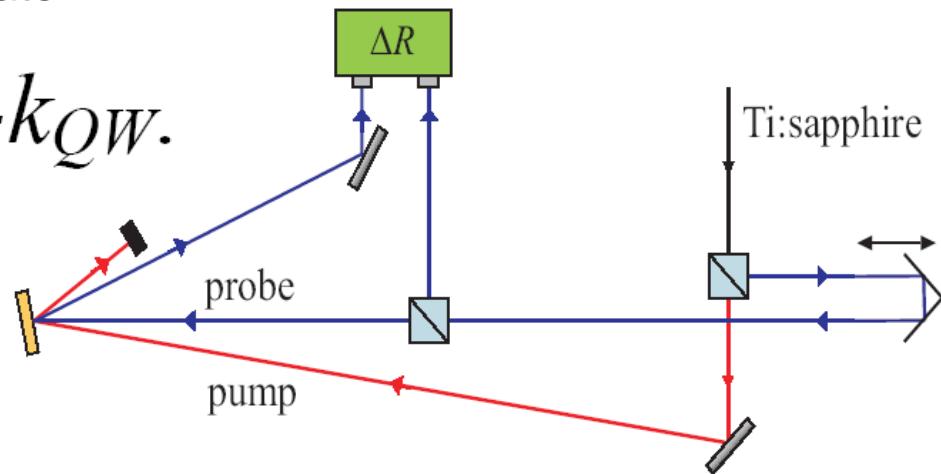


$$\eta = k_{ET} / (k_{ET} + k_{QW})$$

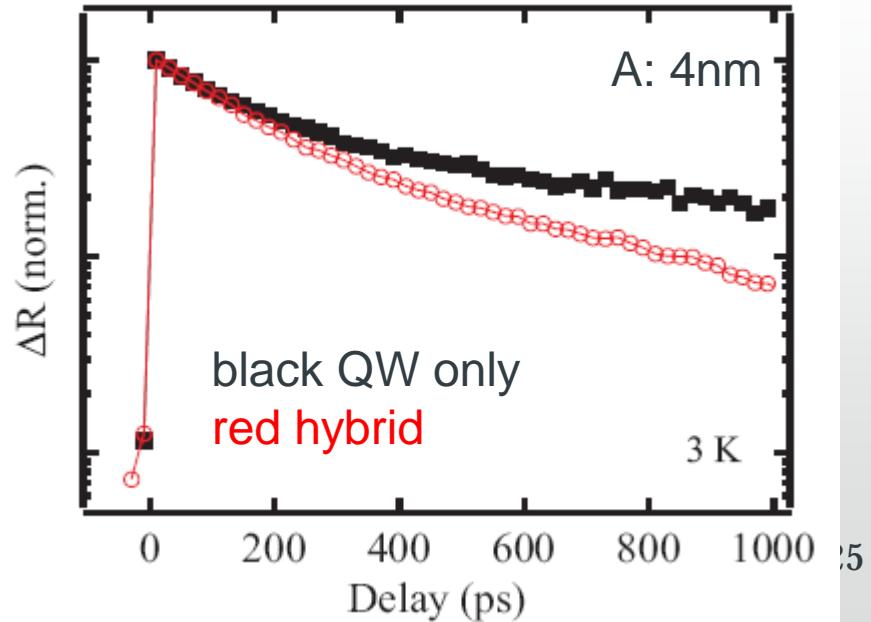
$$\eta_A = 0.23 \text{ and } \eta_B = 0.39$$

$$\Omega_A/\Omega_B = 1.27$$

$$k_A/k_B = 1.18 \pm 0.21$$



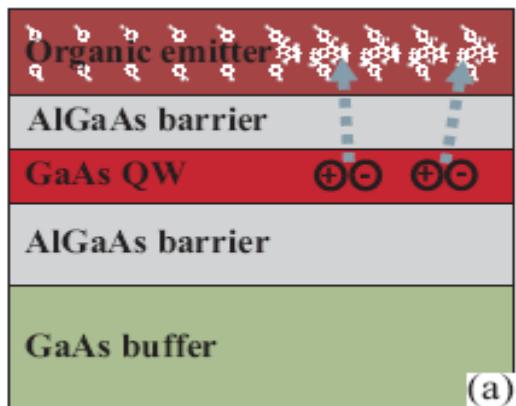
Population decay (photoluminescence)



Hybrid Heterostructures in NIR

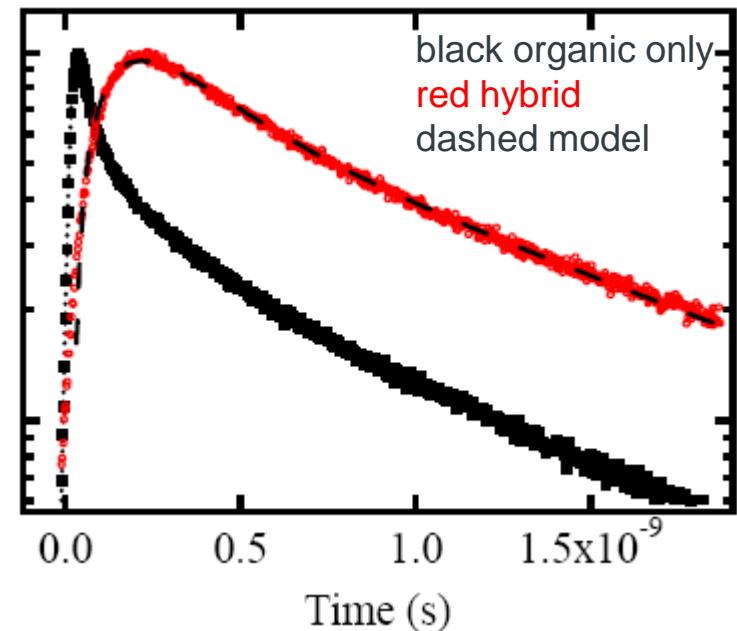
tracking energy transfer at the acceptor site

Time correlated single photon counting



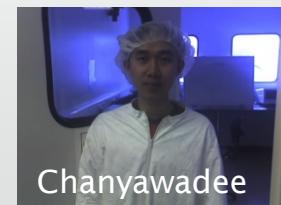
surface states

(a)



Coupled states through non-radiative energy transfer from quantum wells to organic emitter describe transfer dynamics to acceptor (dashed line):

$$I(t) = \sum_{x=1,2} \frac{C_x N_{QW}(t=0) k_{ET}}{k_{OGx} - k_{QW} - k_{ET}} (e^{-(k_{QW} + k_{ET})t} - e^{-k_{QW}t})$$



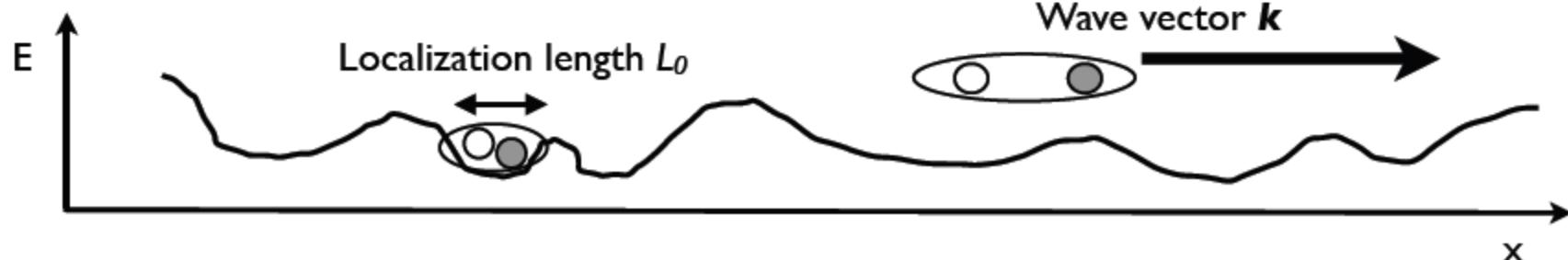
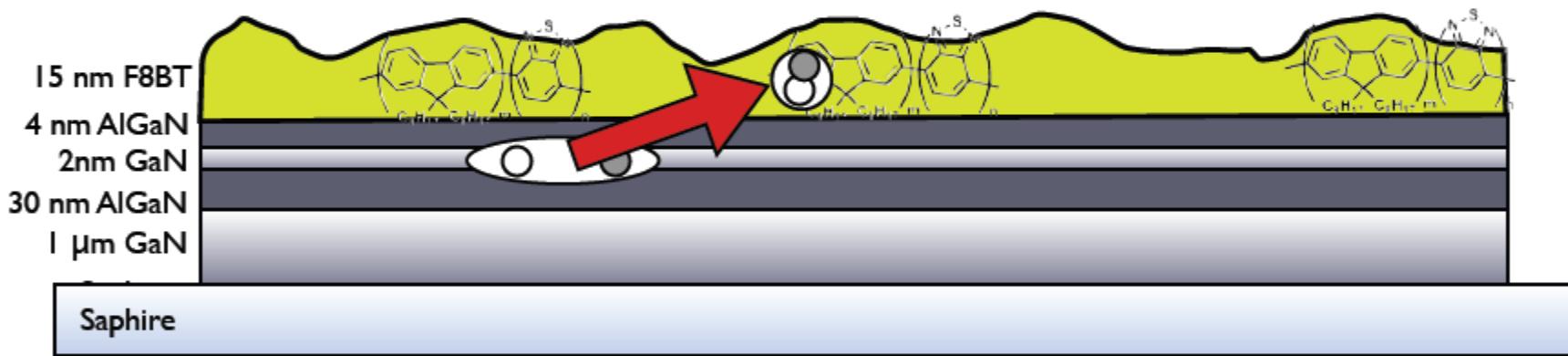
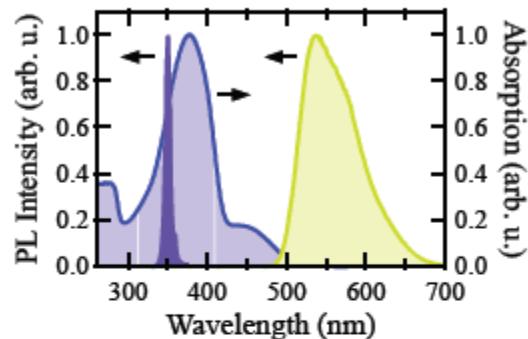
Chanyawadee

all rates are derived from photoluminescence and fluorescence decay measurements

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Testing the concept of dimensionality

- ▶ QW: Wannier-Mott Exciton (donor)
- ▶ F8BT: Frenkel Exciton (acceptor)

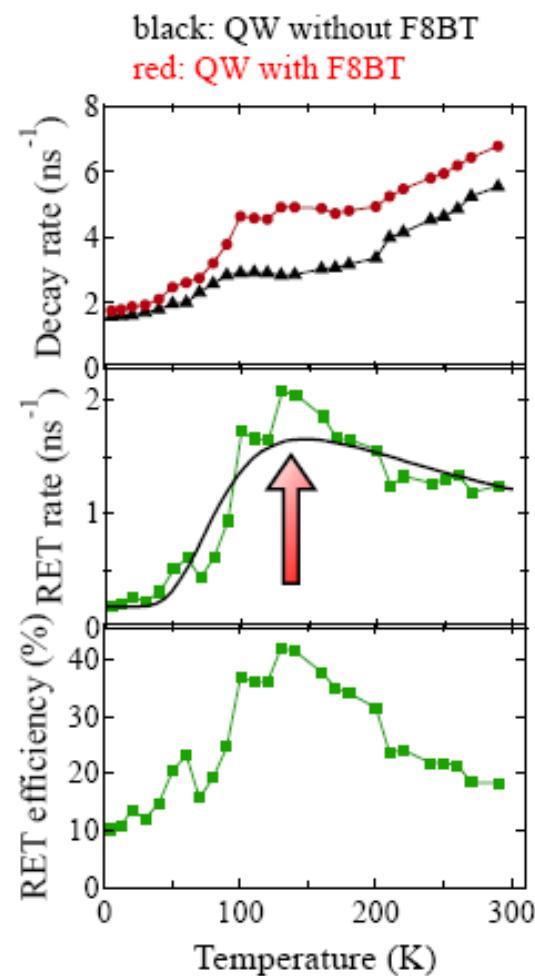


Experimental Results

- RET shows distinct temperature dependence
- 10% RET efficiency at 10 K
43% RET efficiency at 130 K
22% RET efficiency at 300 K
- 0.15% efficiency for emission + absorbtion** at 300 K

$$\eta_{rad} = QY_{QW} \cdot P_{Fresnel} \cdot P_{abs}$$

- Why does RET scale with temperature ?**

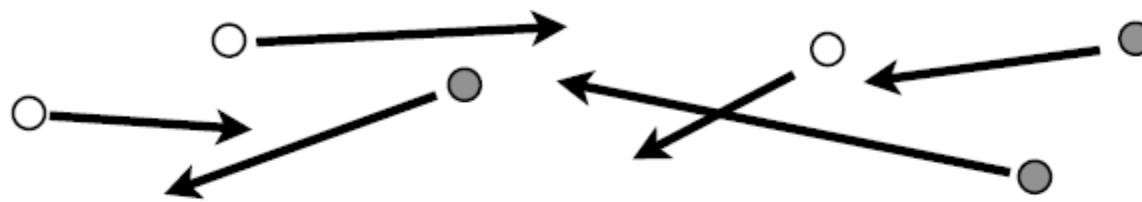


Rindermann, et al., *The Dependence of Resonance Energy Transfer on Exciton Dimensionality*, PRL 107, 236805 (2011)

Rohrmoser et al., *Temperature dependence of exciton transfer in hybrid quantum well/nanocrystal heterostructures*, APL 91, 092126 (2007)

Itskos et al., *Efficient dipole-dipole coupling of Mott-Wannier and Frenkel excitons ...*, PRB 76, 035344 (2007)

Electron-Hole Plasma



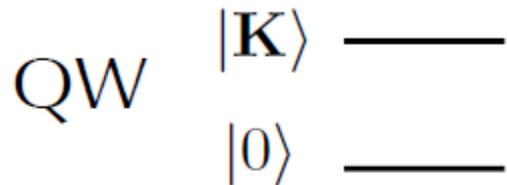
- ▶ ET much slower than relaxation to bound electron-hole pairs (factor 1000)
- ▶ High temperature or high carrier density required

Compare:

Achermann et al., *Energy-transfer pumping of semiconductor nanocrystals using an epitaxial quantum well*, Nature (2004)

Achermann et al., *Different regimes of Förster-type energy transfer between an epitaxial quantum well and a proximal monolayer of semiconductor nanocrystals*, PRB (2005)

Resonance Energy Transfer

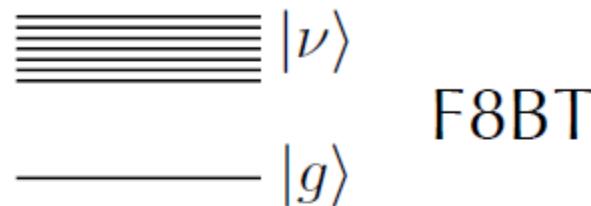
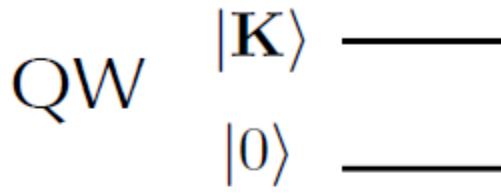


- ▶ Dipole moment d_{vc} for transition from conduction band to valence band
- ▶ QW Polarization

$$\hat{P}_{QW}(\mathbf{r}) = d_{vc} \psi(\mathbf{r}_e, \mathbf{r}_h) \Big|_{\mathbf{r}_e = \mathbf{r}_h = \mathbf{r}} |0\rangle \langle \mathbf{K}| + \text{h.c.}$$

produces electric field $\hat{\mathbf{E}}$

Resonance Energy Transfer



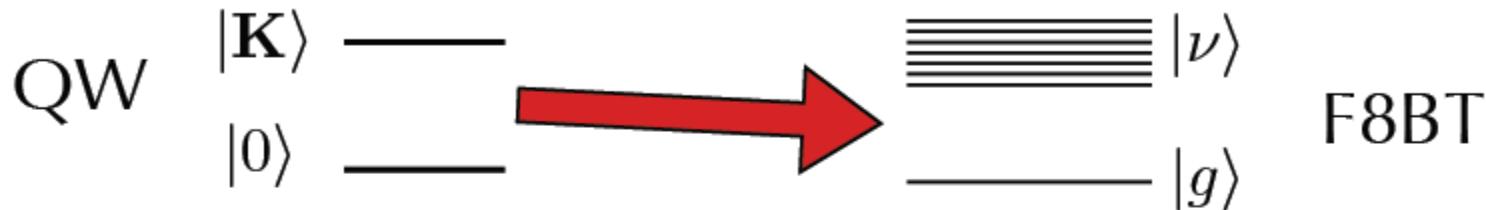
- Dipole moment d_{vc} for transition from conduction band to valence band
- QW Polarization

$$\hat{P}_{QW}(r) = d_{vc} \psi(r_e, r_h) \Big|_{\substack{r_e = r \\ r_h = r}} |0\rangle \langle K| + \text{h.c.}$$

produces electric field $\hat{\mathbf{E}}$

- Dipole moment between excited and ground state
- Polarization \hat{P}_{org} subject to electric field produced by QW polarization

Resonance Energy Transfer



- Dipole moment d_{vc} for transition from conduction band to valence band

- QW Polarization

$$\hat{P}_{QW}(r) = d_{vc} \psi(r_e, r_h) \Big|_{\substack{r_e = r_h = r}} |0\rangle \langle K| + \text{h.c.}$$

produces electric field $\hat{\mathbf{E}}$

- Dipole moment between excited and ground state

- Polarization \hat{P}_{org} subject to electric field produced by QW polarization

$$\hat{H}_{int} = - \int d^3R (\hat{P}^{org}(R) \cdot \hat{\mathbf{E}}(R))$$

= interaction Hamiltonian for Resonance Energy Transfer (QM)

= power dissipated in organic medium in presence of classical oscillating polarization inside QW (classical)

$$\Gamma_{RET} = \frac{2\pi}{\hbar} |\hat{H}_{int}|^2$$

= rate of Resonance Energy Transfer

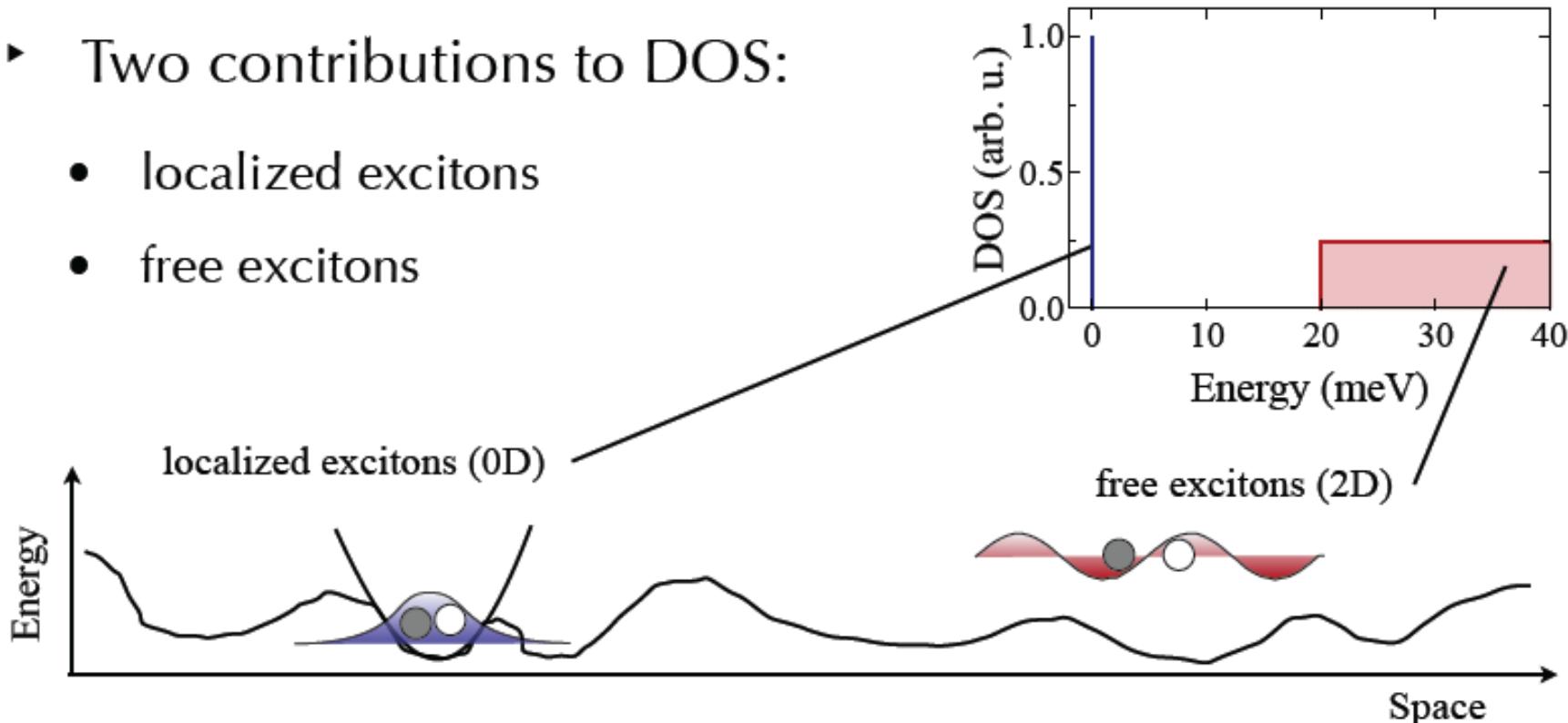
Energy transfer in the exciton ensemble

- Effective RET rate in the exciton ensemble:

$$\langle \Gamma_{RET} \rangle_{ens} = \frac{1}{Z(T)} \int_0^{\infty} \Gamma_{RET}(E) \cdot DOS(E) \cdot e^{-E/k_B T} dE$$

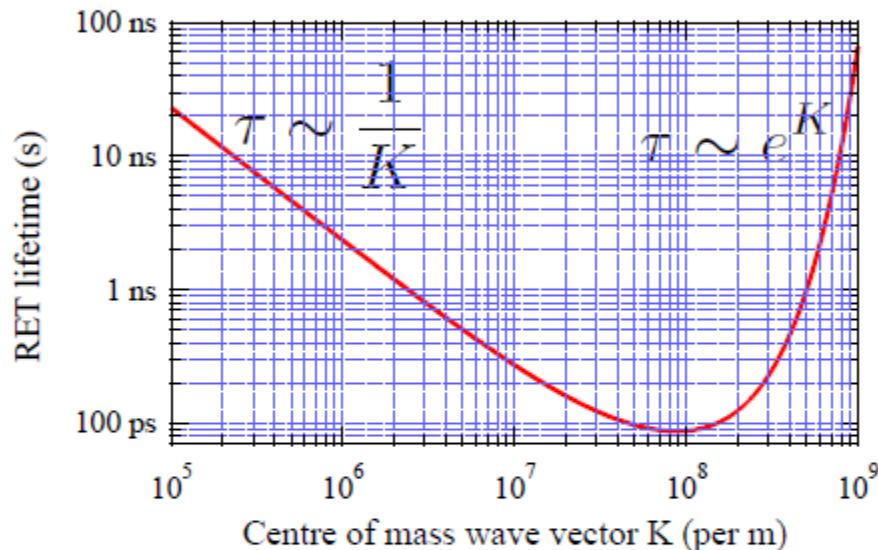
- Two contributions to DOS:

- localized excitons
- free excitons



Free Excitons

- ▶ Kinetic Energy determines k -vector

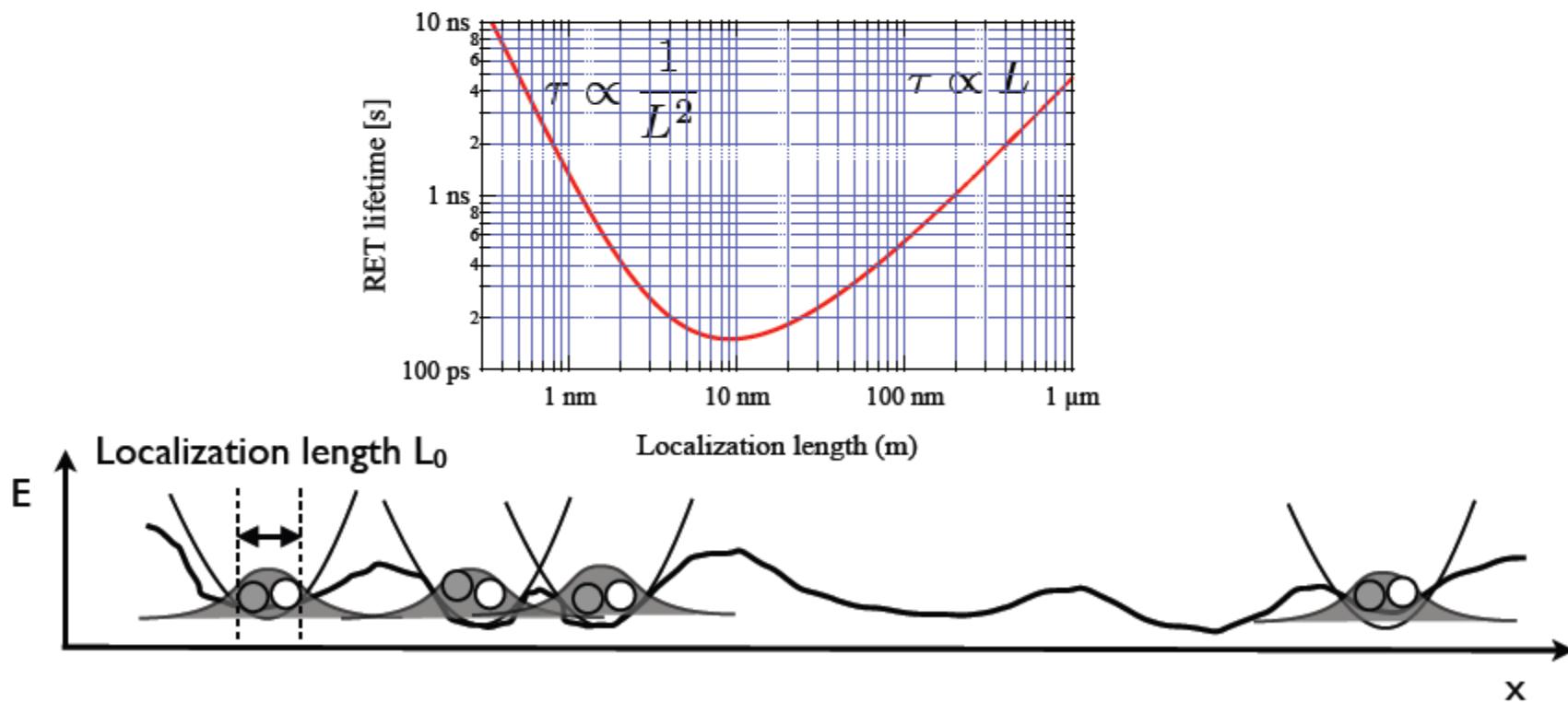


- ▶ Compare: dipolar interaction between two planes
- ▶ Rate of RET changes dramatically with k -vector

$$V(K, d) \propto K e^{-Kd}$$

Localized Excitons

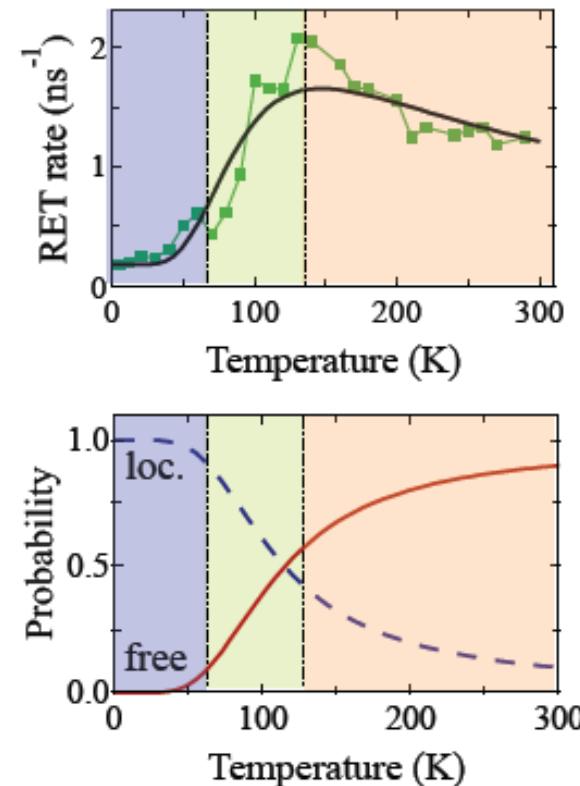
- ▶ Assumption: excitons trapped in 2D isotropic parabolic wells
- ▶ Decomposition of wave-function into plane-waves with different wave vectors



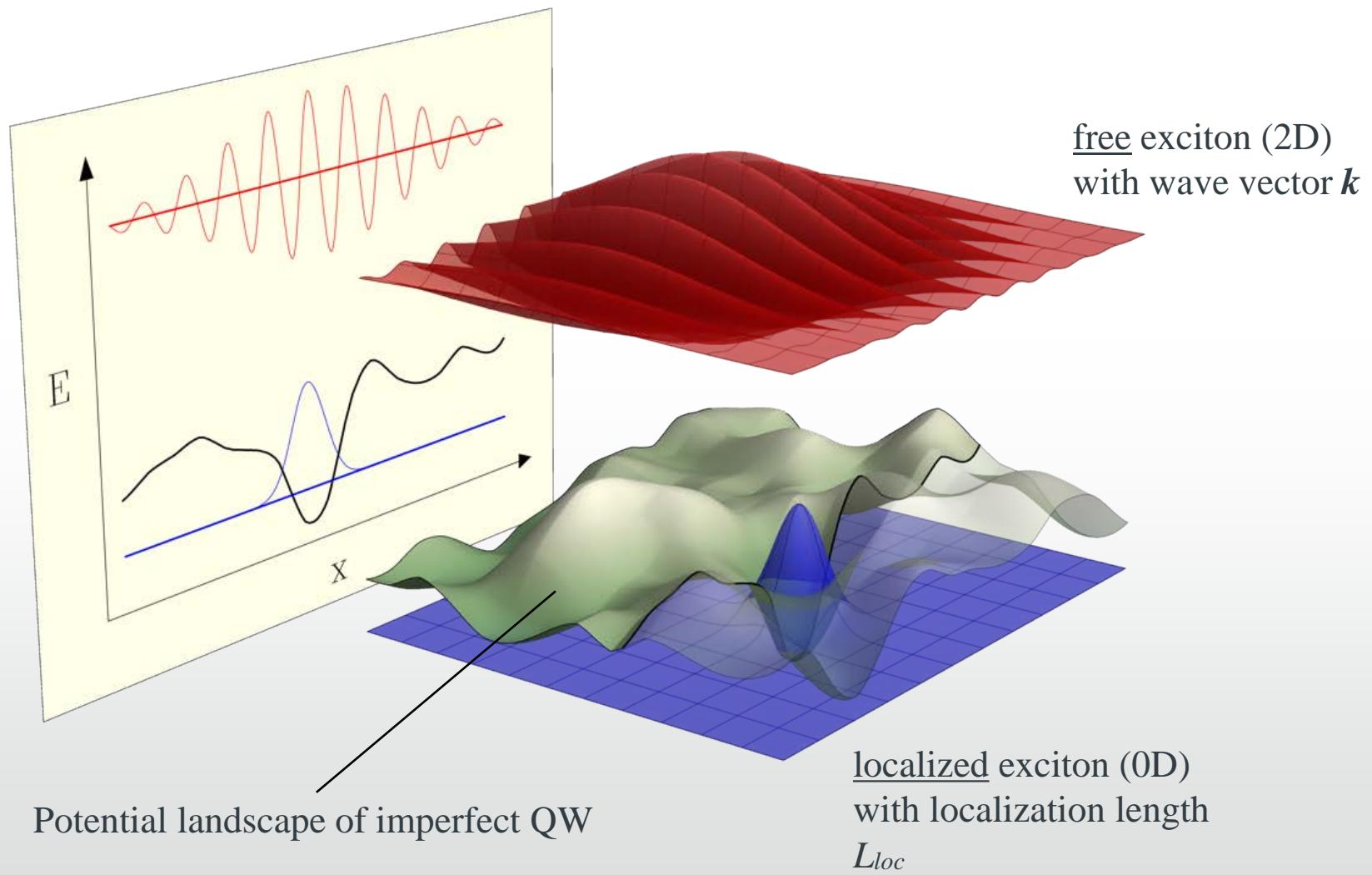
Simulation vs Experiment

$$\langle \Gamma_{RET} \rangle_{ens} = \frac{1}{Z(T)} \int_0^{\infty} \Gamma_{RET}(E) \cdot DOS(E) \cdot e^{-E/k_B T} dE$$

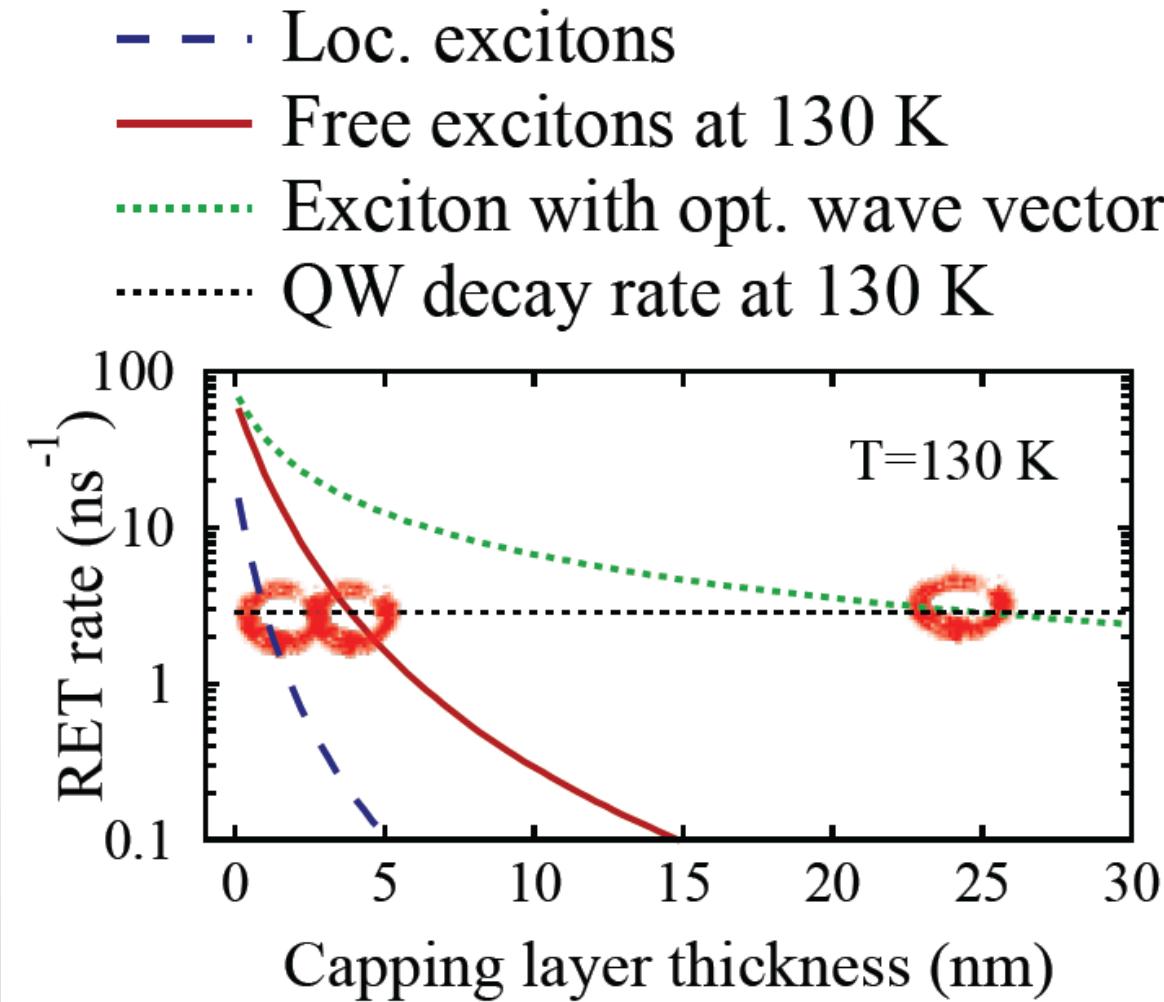
- Temperature dependent balance between localized and free excitons
- RET depends on exciton dimensionality: 0D vs. 2D excitons
- Experimentally observed temperature dependence reproduced with 3 parameters:
 - $V_{trap} = 20 \text{ meV}$
 - $L_{loc} = 0.9 \text{ nm}$ (compare average spacing Al atoms: 2nm)
 - Area density of traps = $4 \cdot 10^{11} \text{ cm}^{-2}$



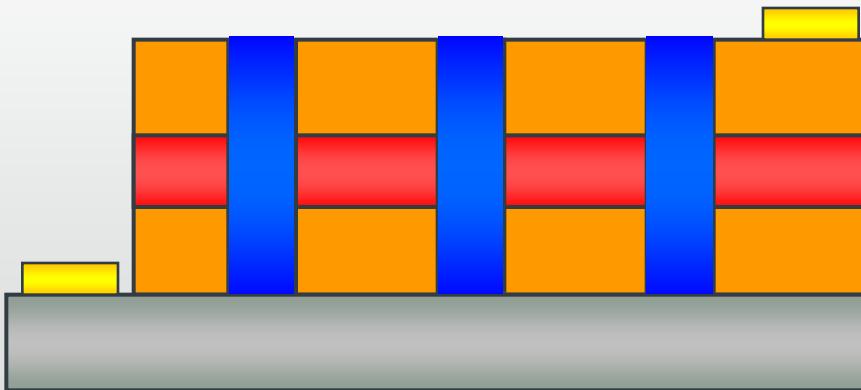
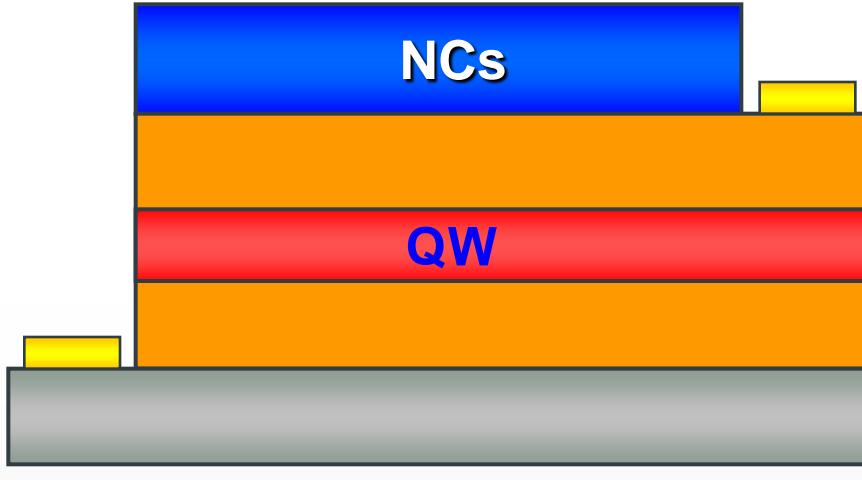
Excitons in the QW potential landscape



Resonance Energy transfer vs exciton localisation



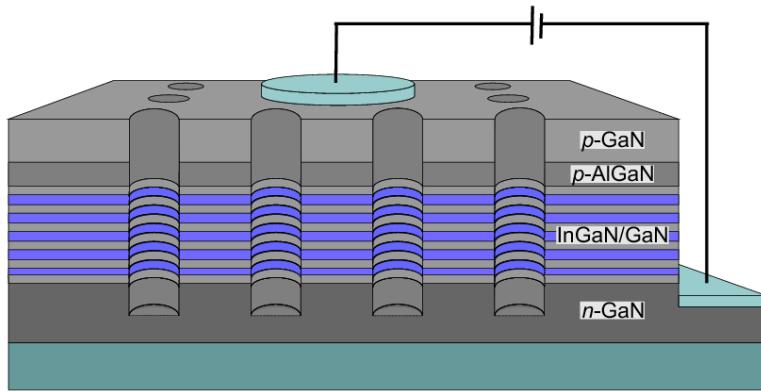
Hybrid QD/QW structure



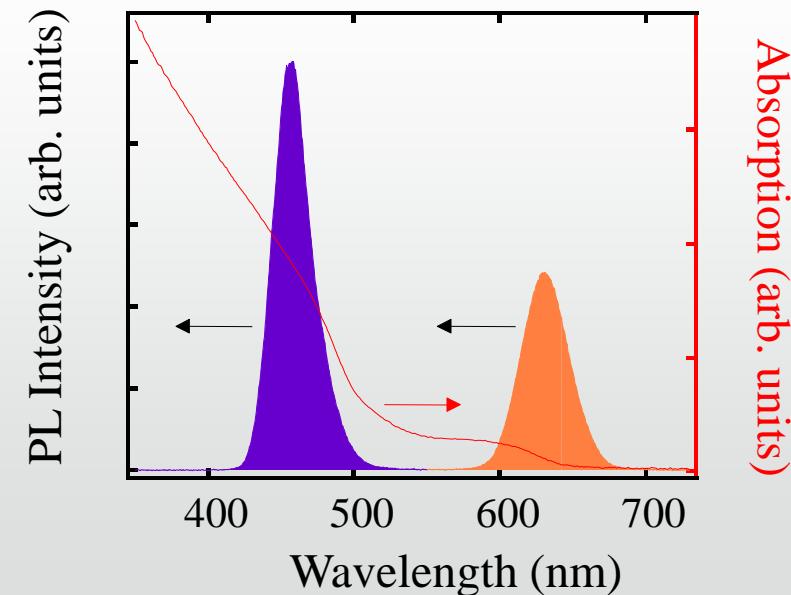
- energy transfer rate $\propto R^{-n}$
- minimum barrier width

- patterned QW
- shorter donor-acceptor distance

Hybrid colour conversion LED

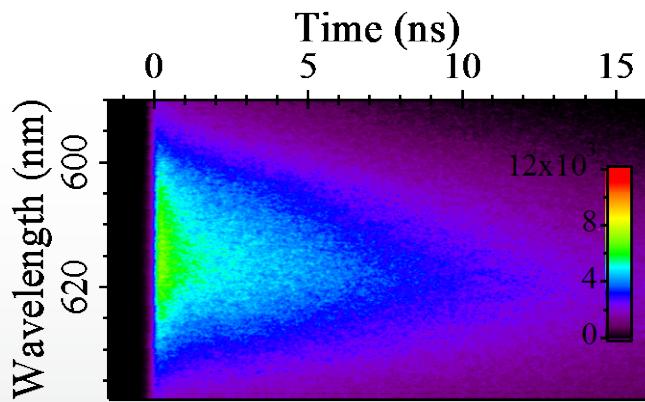


- Surface-textured LEDs
PL peak @ 457 nm
- Colloidal QDs
FL peak @ 618 nm

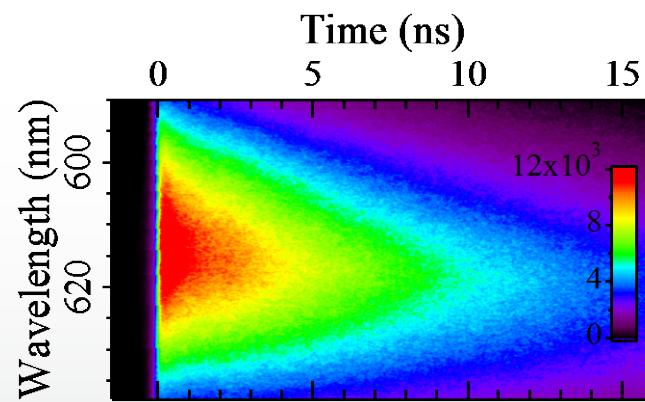


Fluorescence decay of QDs

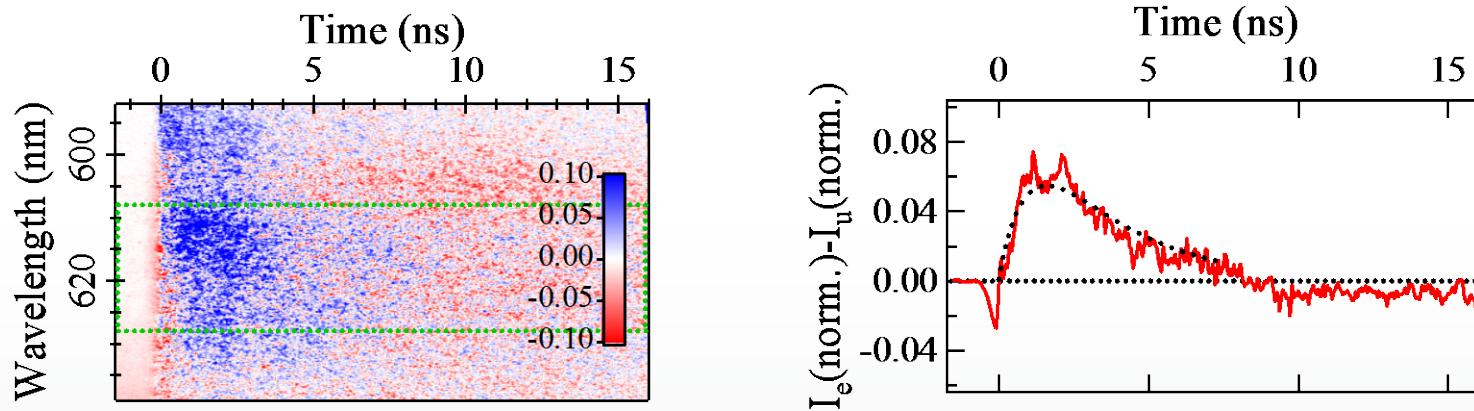
Unetched QWs: no RET



Etched QWs: RET enabled



Fluorescence decay of QDs

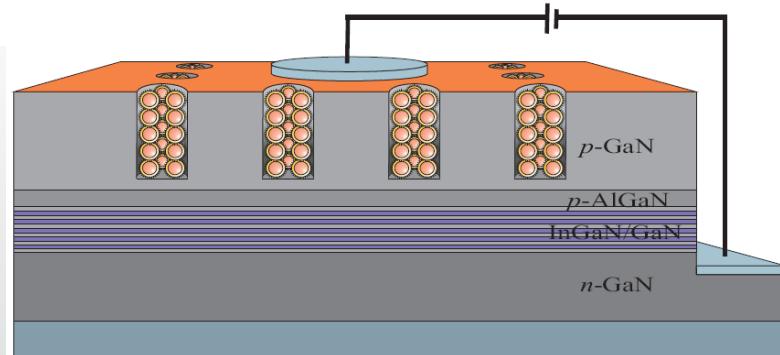


$$I(t) \propto \frac{k_{ET}}{k_{NC} - k_{QW} - k_{ET}} (e^{-(k_{QW} + k_{ET})t} - e^{-k_{NC}t})$$

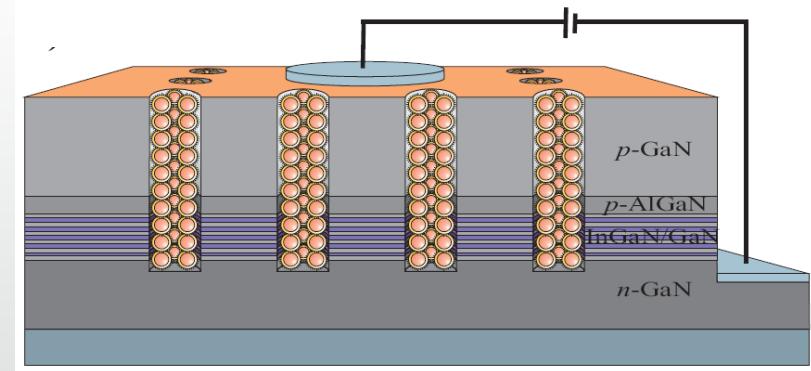
Carrier injection due to nonradiative energy transfer

Increased Color-Conversion Efficiency in Hybrid Light-Emitting Diodes utilizing Non-Radiative Energy Transfer

By Soontorn Chanyawadee, Pavlos G. Lagoudakis,* Richard T. Harley,
Martin D. B. Charlton, Dmitri V. Talapin, Hong Wen Huang, and
Chung-Hsiang Lin



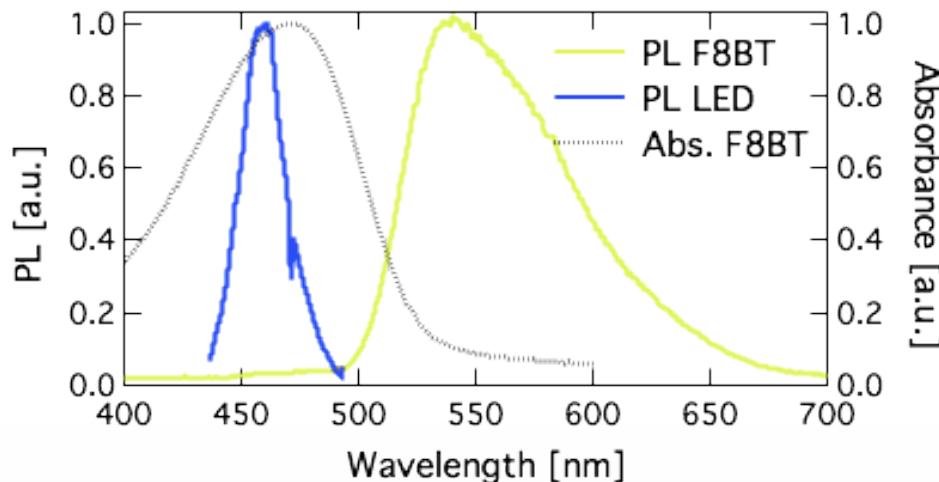
Unetched QWs + QDs



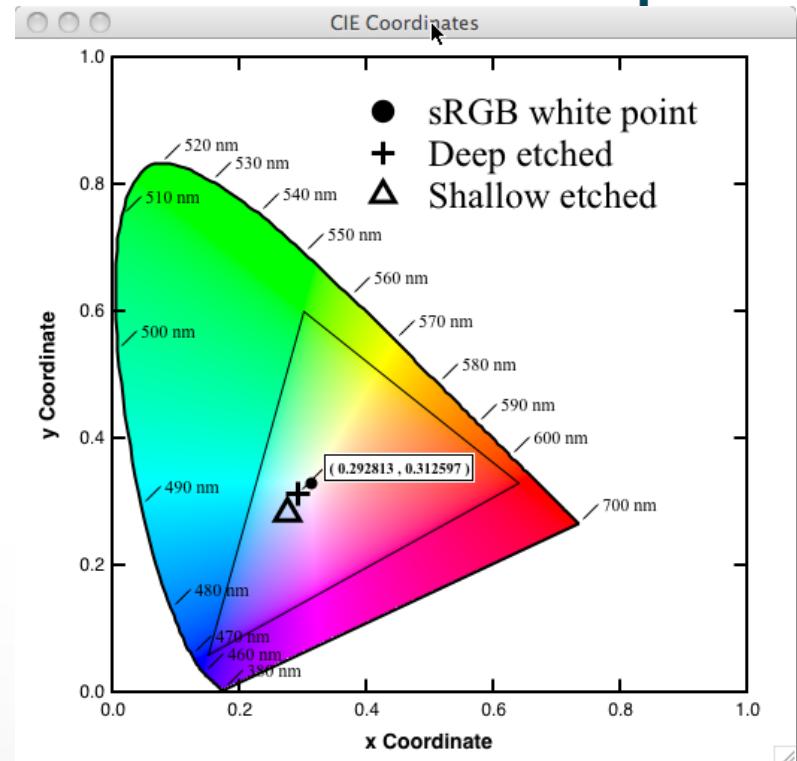
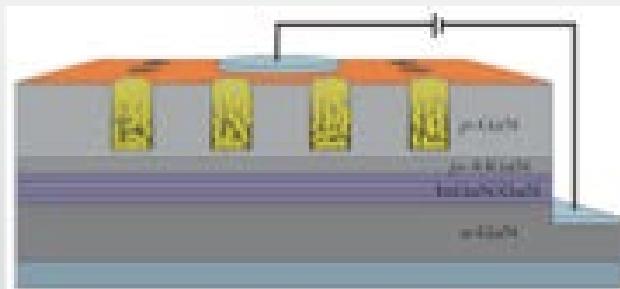
Etched QWs + QDs



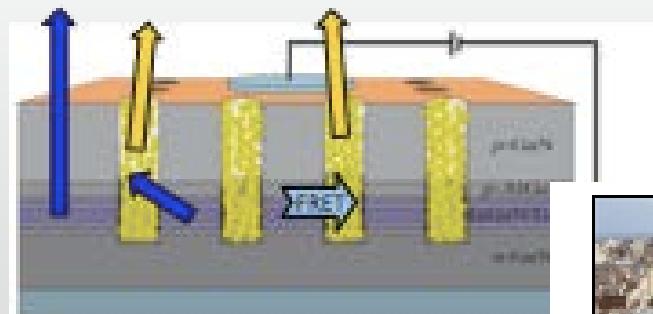
Hybrid LED with F8BT



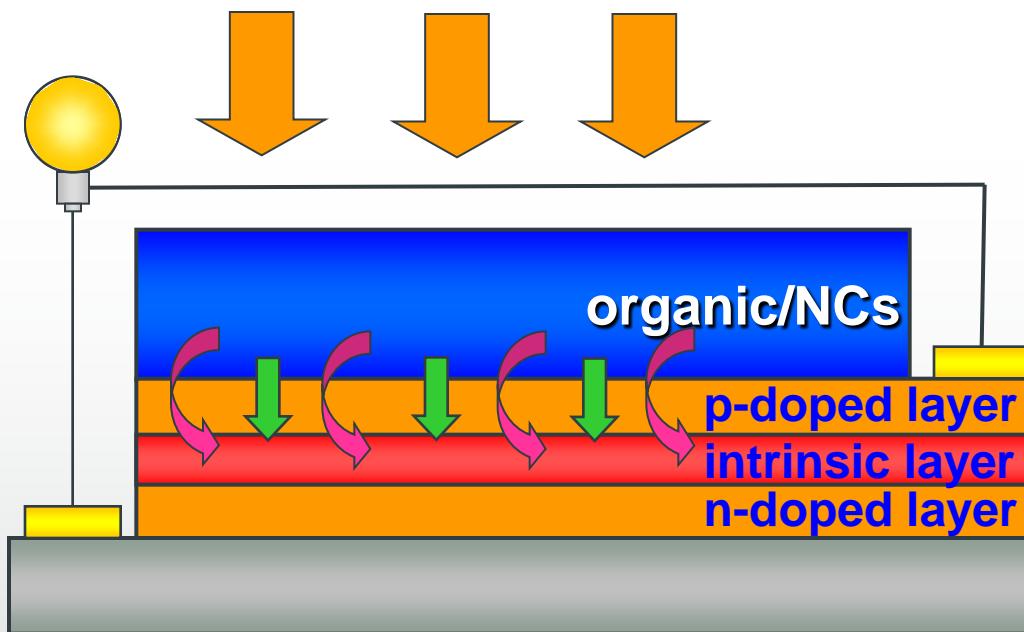
shallow-etched LED



deep-etched LED



Hybrid photovoltaics



Carrier generation

- QD layer

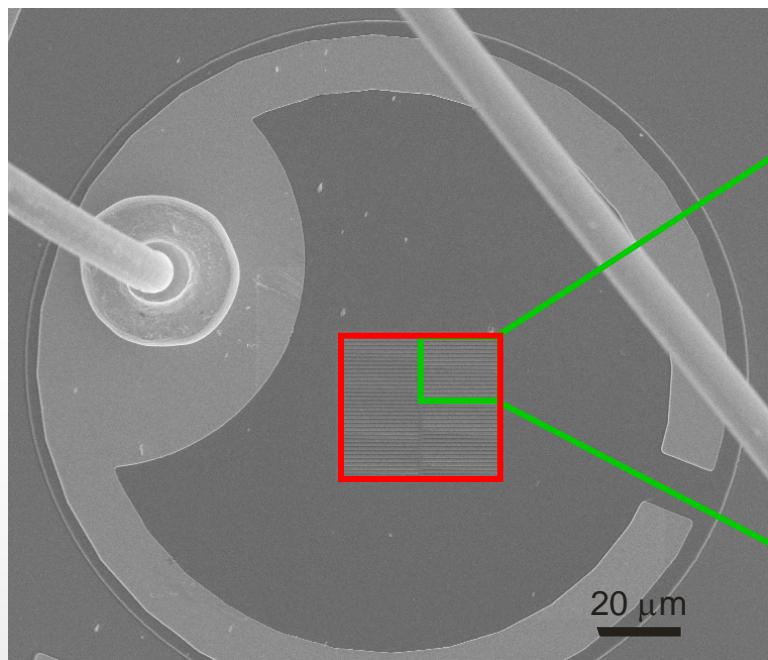
Energy transfer

- Radiative energy transfer
- Nonradiative energy transfer

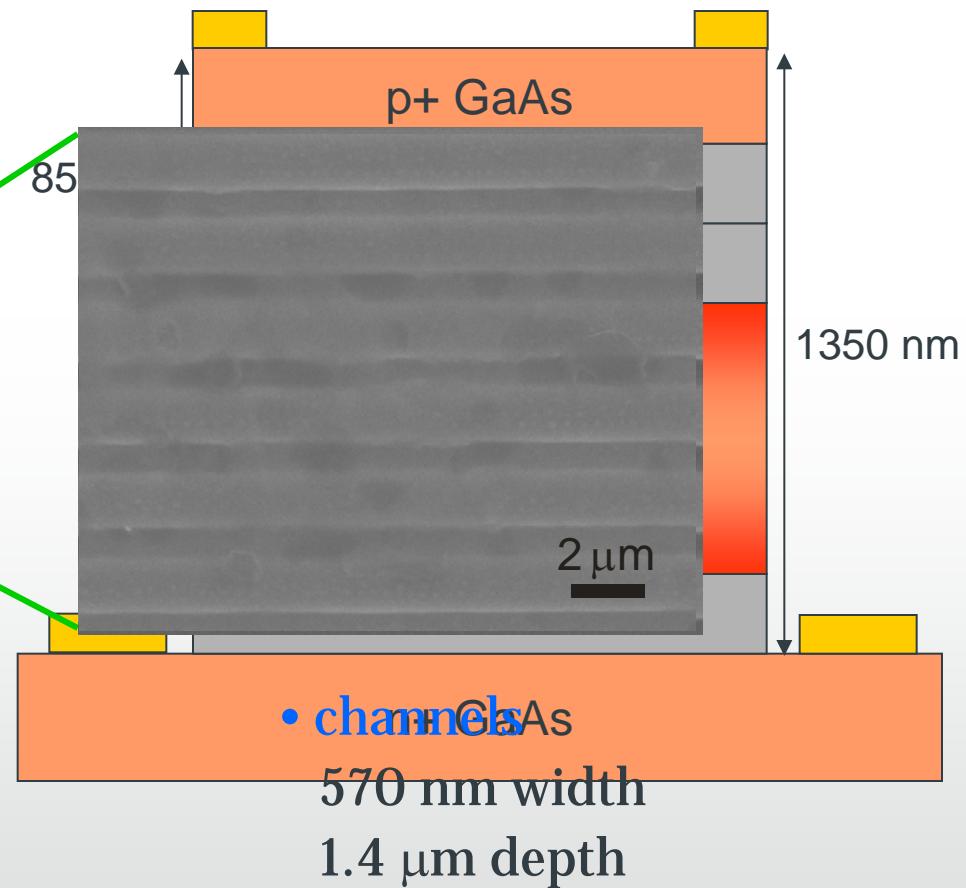
Carrier extraction

- pin heterostructure

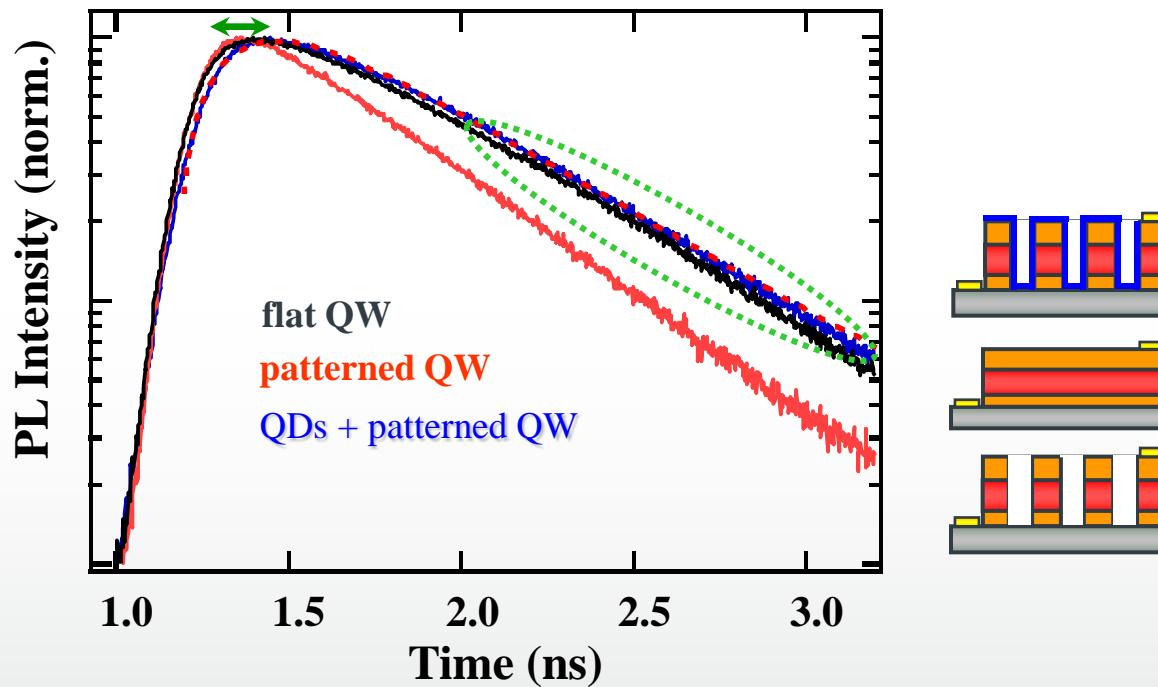
Hybrid QD/patterned QW structure



- $80 \times 80 \text{ mm}^2$ pattern

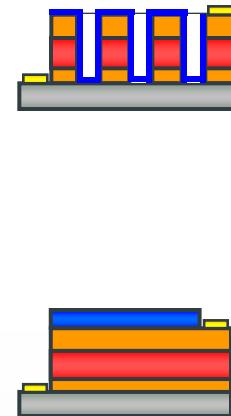
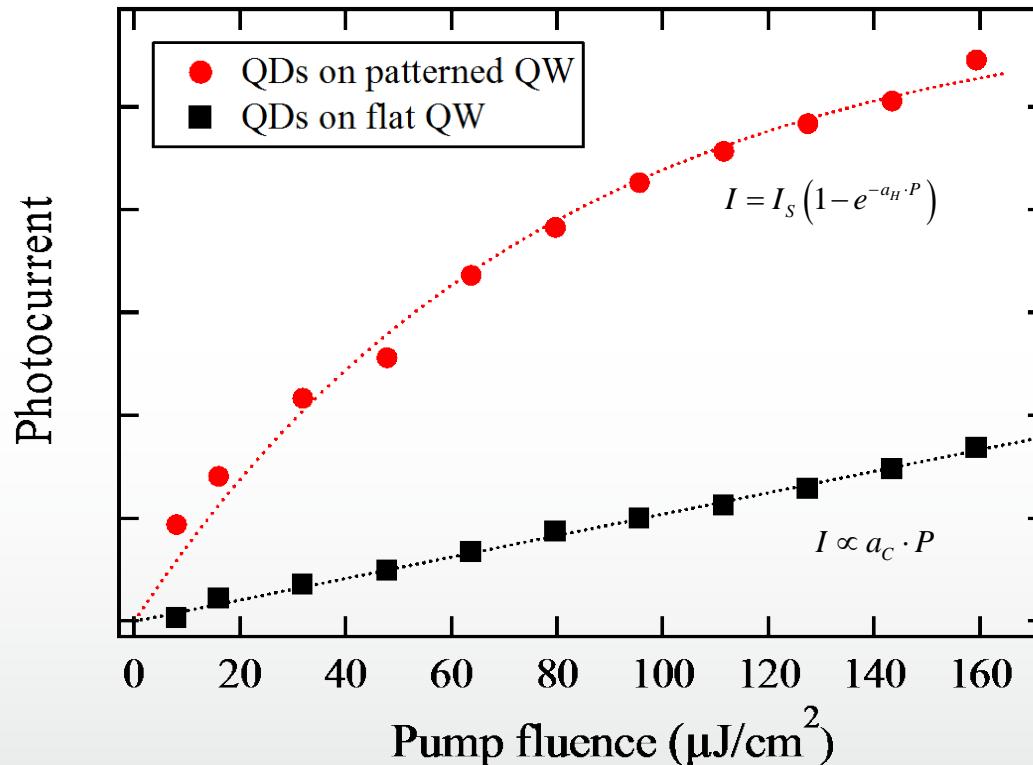


Photoluminescence decay of QWs

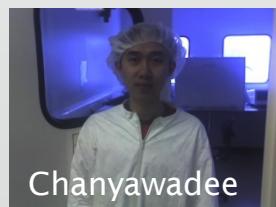


- Longer rise time indicates energy transfer
- $I(t) = \frac{n_{QDi}(0)k_{ETi}}{k_{QW}k_{QDi}k_{ETi}}(e^{-(k_{QDi}+k_{ETi})t} - e^{-k_{QW}t}) + f(t)$

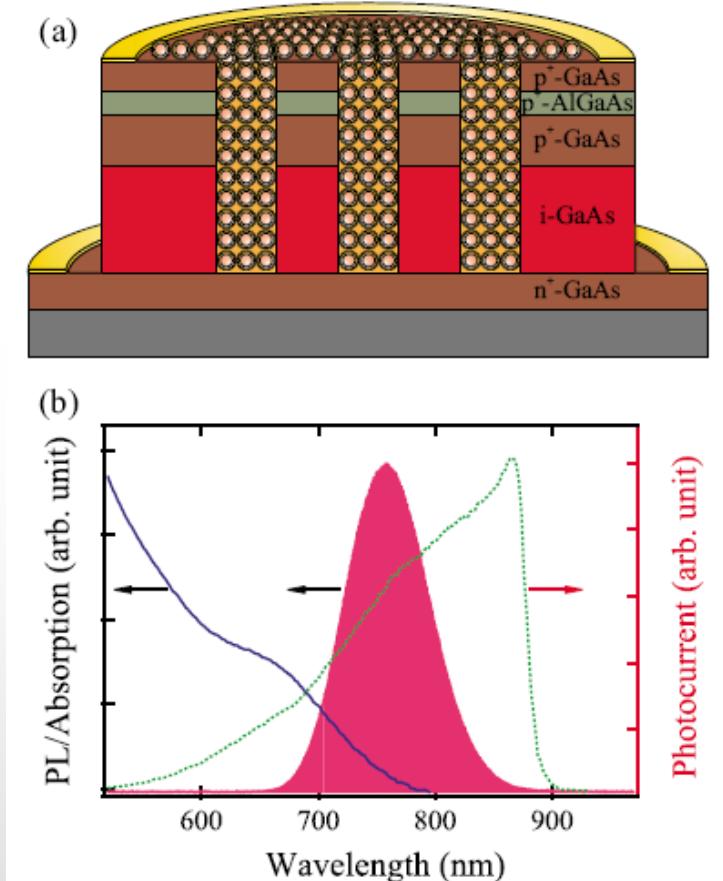
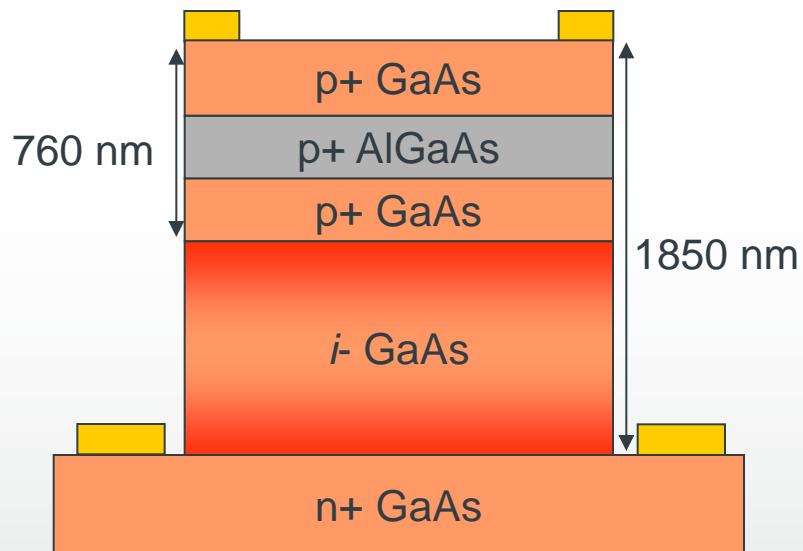
Photocurrent conversion efficiency



- 6-fold enhancement of photocurrent conversion efficiency
- 64% generated from nonradiative energy transfer

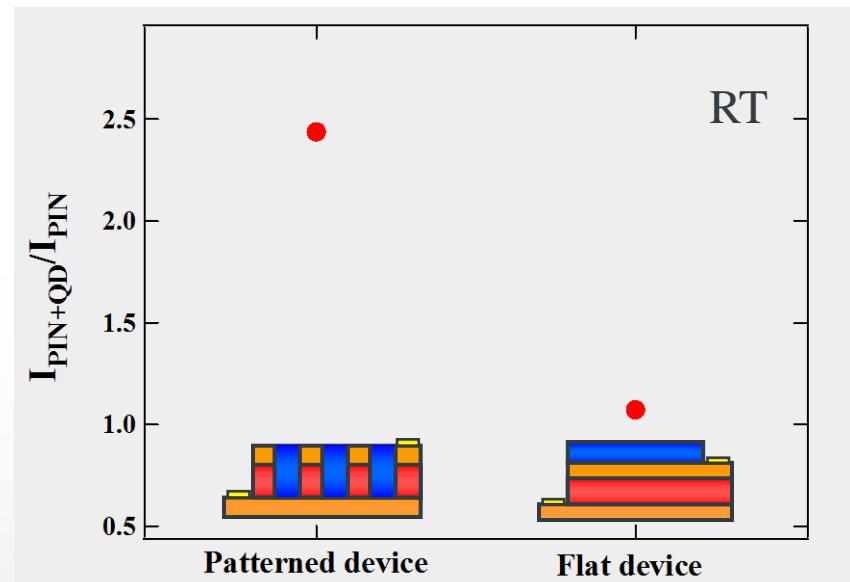
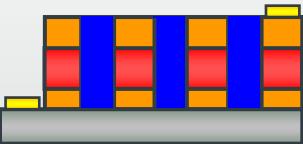
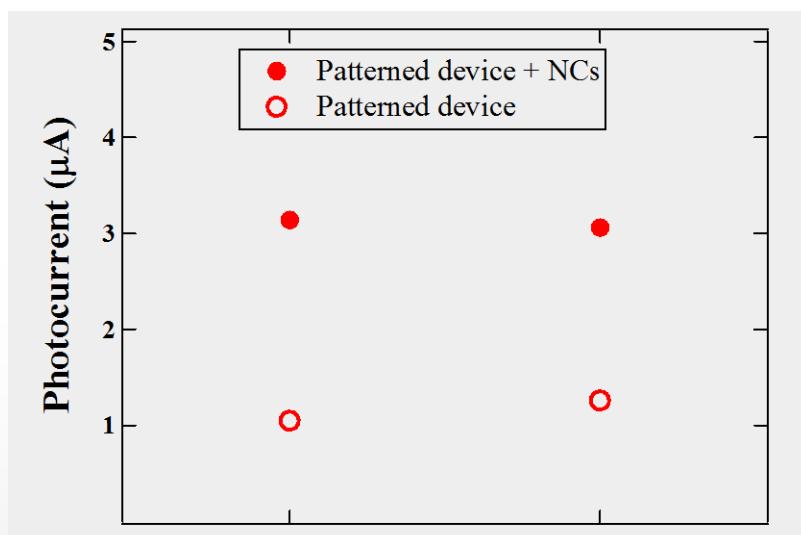


Hybrid NC/patterned bulk GaAs device



- photoluminescence peak of CdTe NCs : 734 nm
- PIN device : 823 nm

Hybrid NC/patterned bulk GaAs device



- photocurrent increases in hybrid structures
- photocurrent enhancement is higher in patterned device

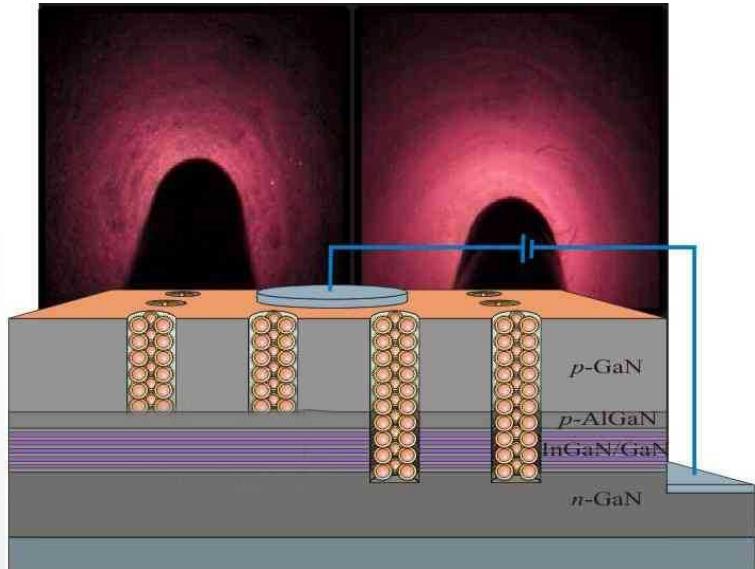
Outlook: RET optoelectronic devices

Photovoltaics

- Silicon HPVs (TSMC), surface treatment, organic sem., blends

Lighting application

- surface passivation/surface-textured LEDs, organic phosphors, organic/QD lasers



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- Optical spectroscopy
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