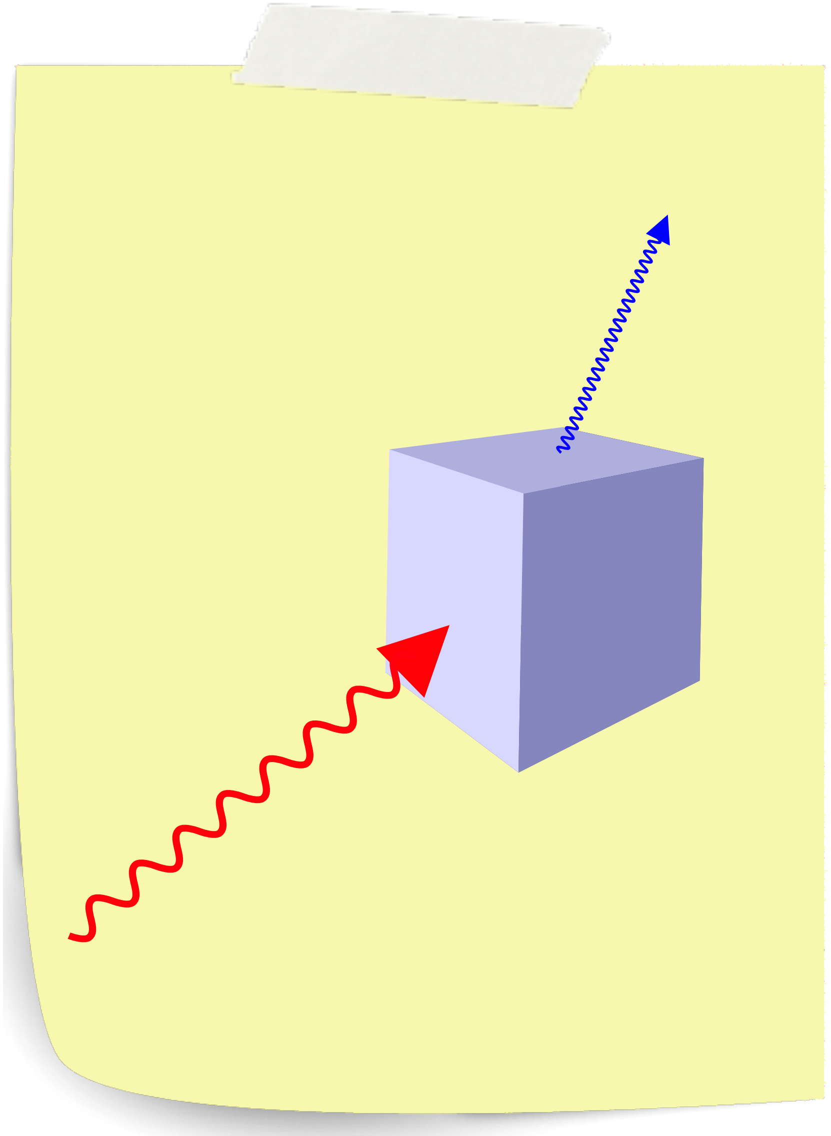
Sensitized Upconversion

Jochen Zimmermann, Roberto Mulet, Thomas Wellens,
Greg D. Scholes, and Andreas Buchleitner

Fundamental Problems in Quantum Physics
Erice, March 25, 2015

Motivation

Upconversion: Generation of photons with higher energy



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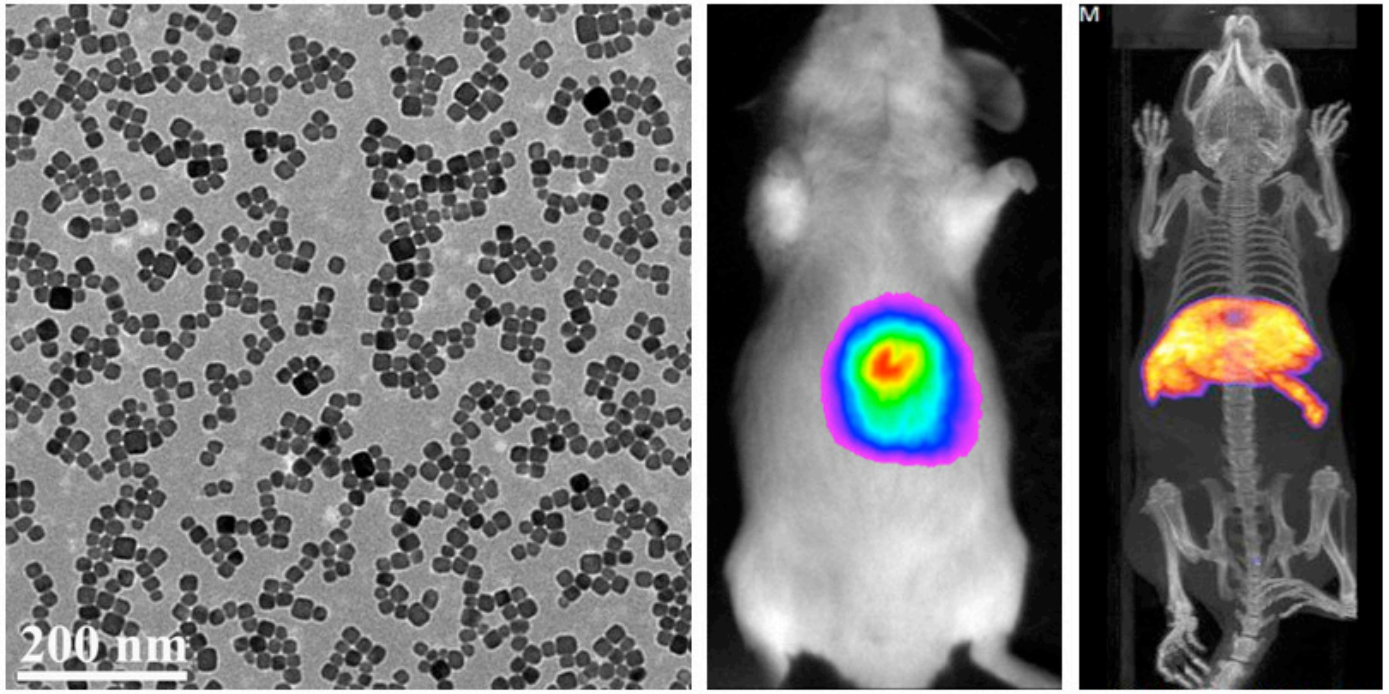
Upconversion: Generation of photons with higher energy

Applications:

- Light harvesting
- Bio imaging[1]
- 3D displays[2]
- Temperature sensing



1 Liu et al., **J. Am. Chem. Soc. (2012)**, 134, 5390
2 Miteva et al., **NJP (2008)**, 10, 103002

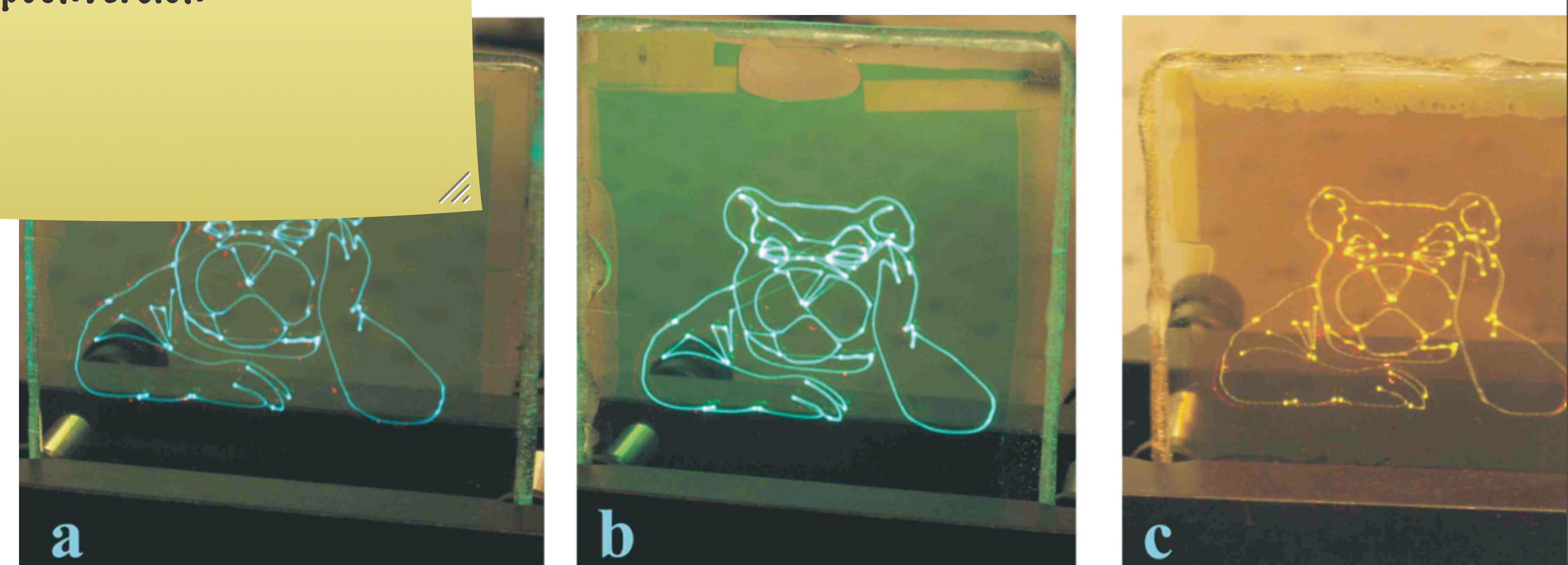
Motivation

Upconversion: Generat
photons with higher en

temp sensing with sub
mum resolution,
intensity ratio of
phosphorescence and
upconversion

Applications:

- Light harvesting
- Bio imaging[1]
- 3D displays[2]
- Temperature sensing



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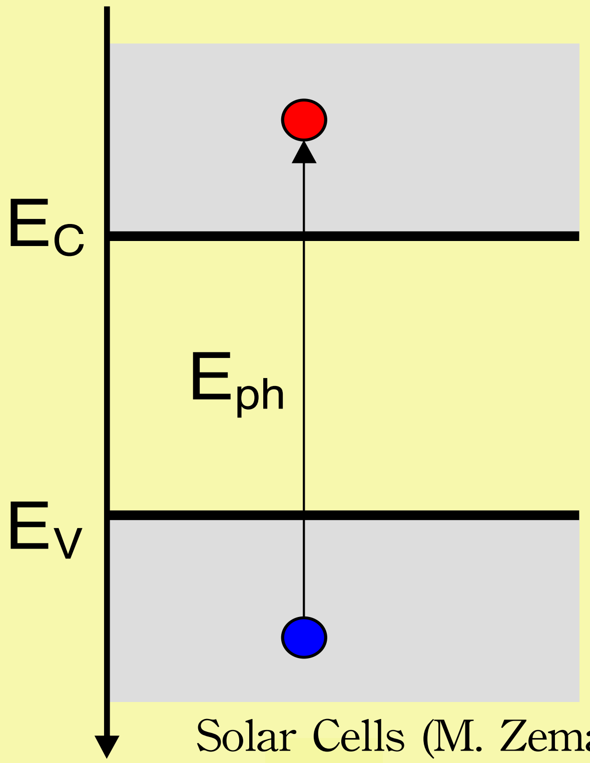
Limits to Conventional Solar Light Harvesting



Solar Cells (M. Zeman)

- minimal absorption energy
- thermal losses

1 Briggs et al., J. Appl. Phys. **(2013)**, 113, 124509

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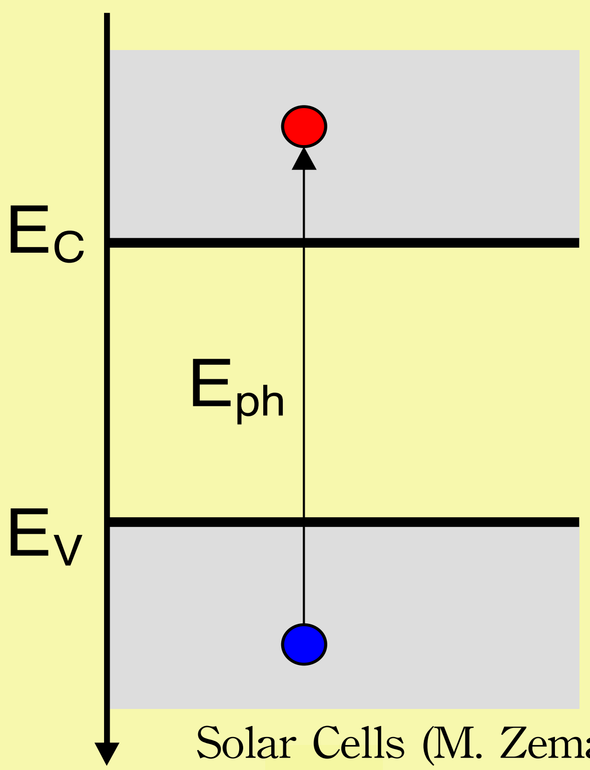

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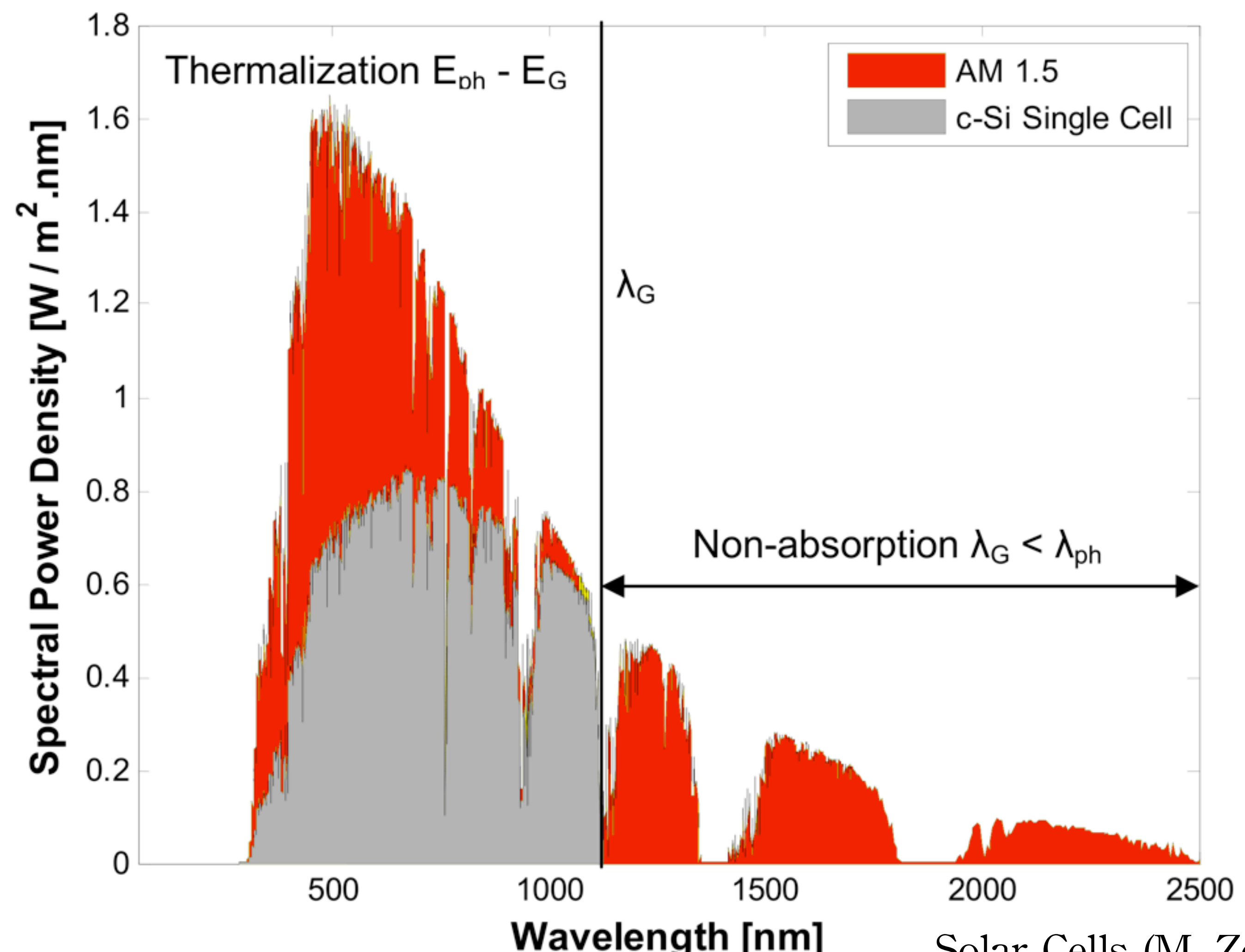

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- photons in NIR are not used
- real devices achieve ~25% efficiency

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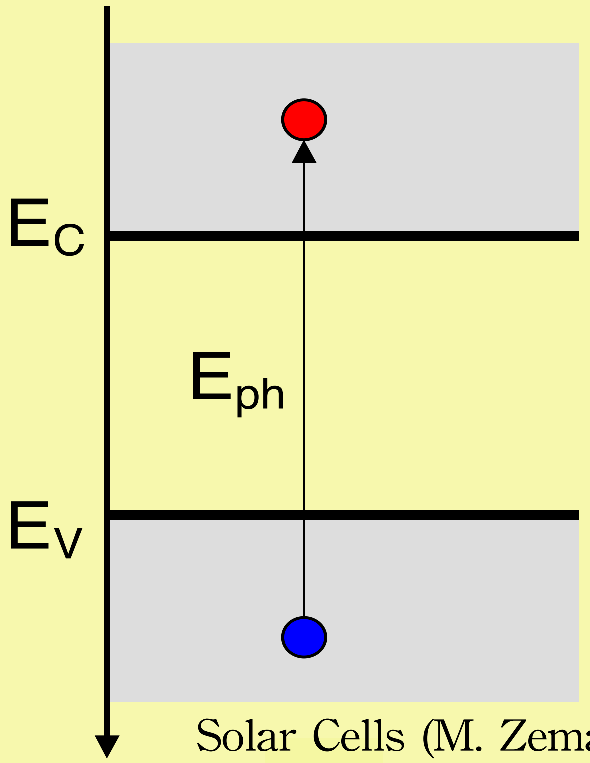

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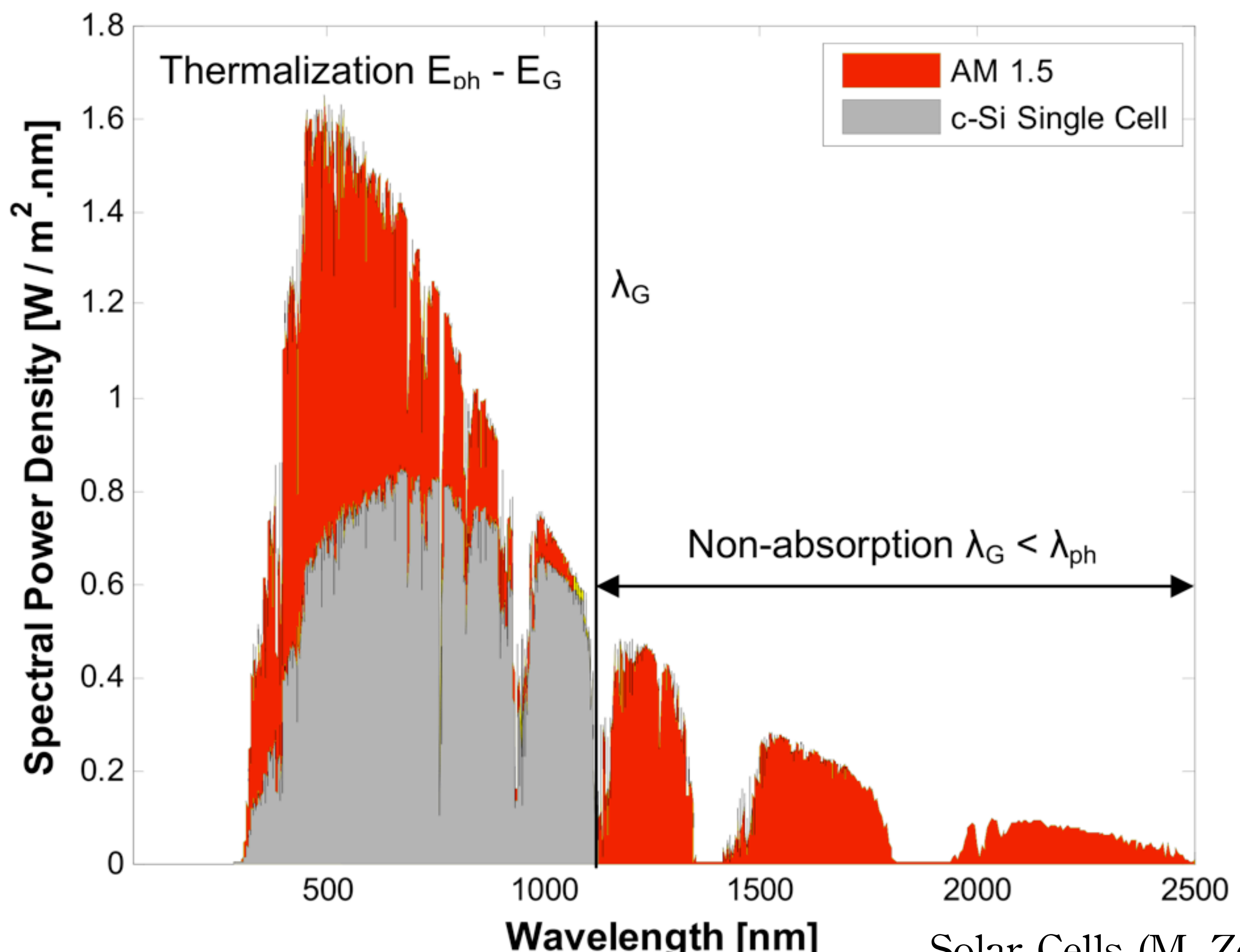

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  - increase to ~35% possible[1]

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Solution: Upconvert NIR Photons

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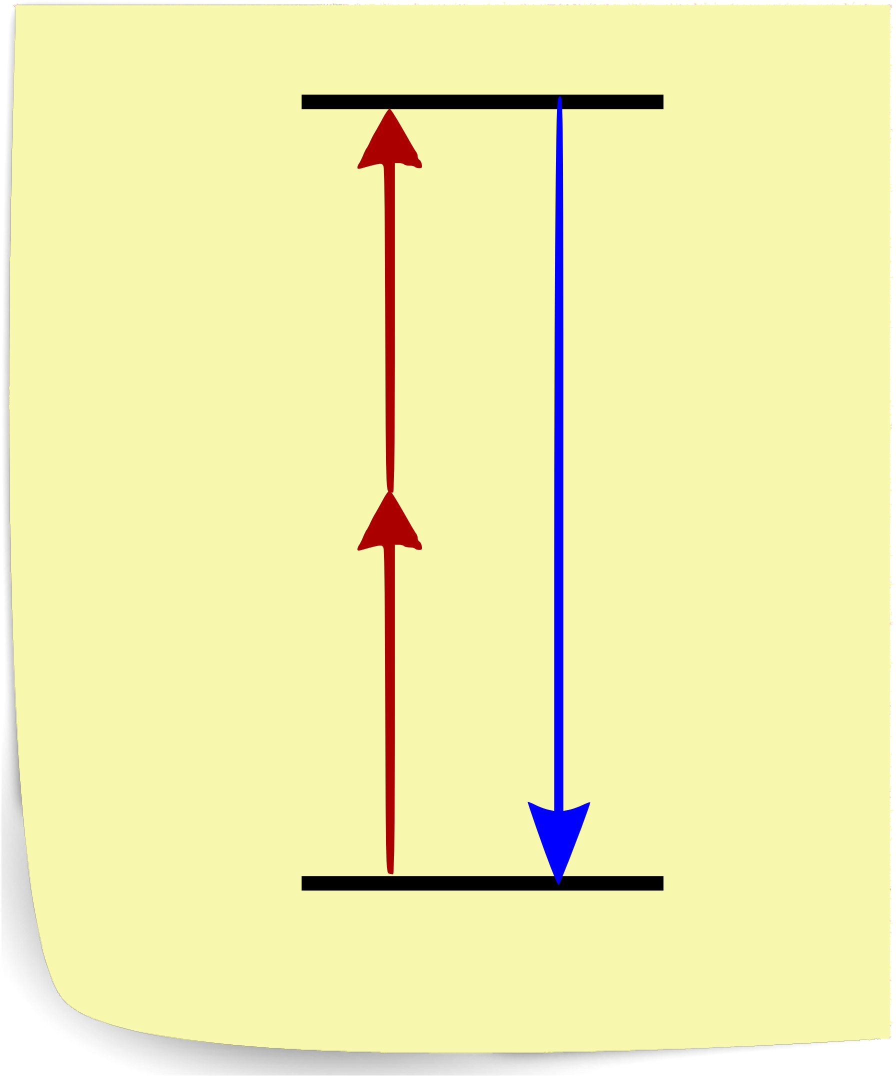

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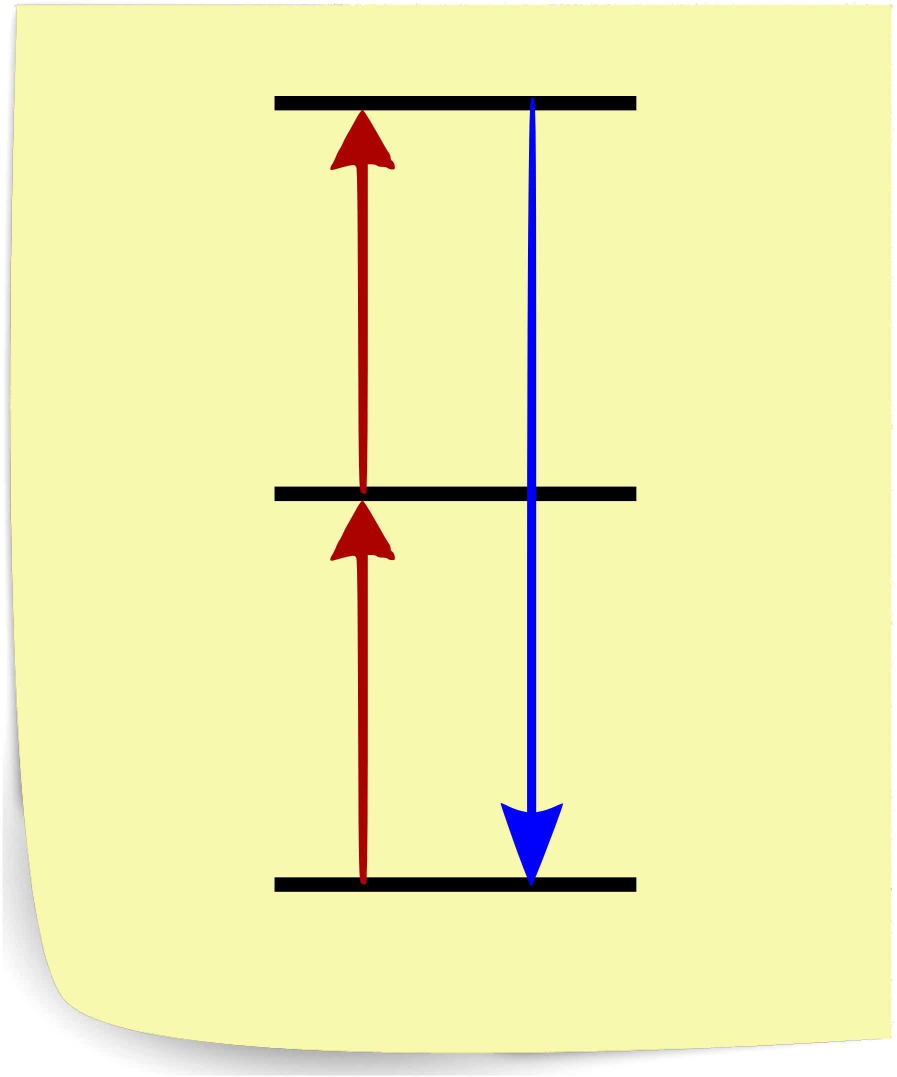

Solution: Upconvert NIR Photons

conventional upconversion requires high intensity

$$\sim I(\omega)^2$$

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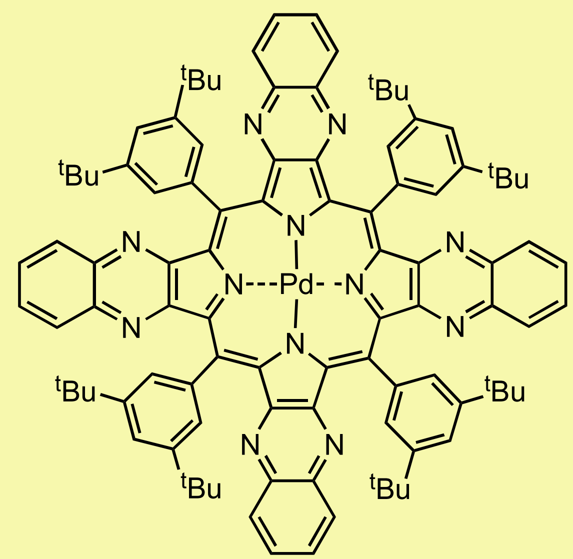
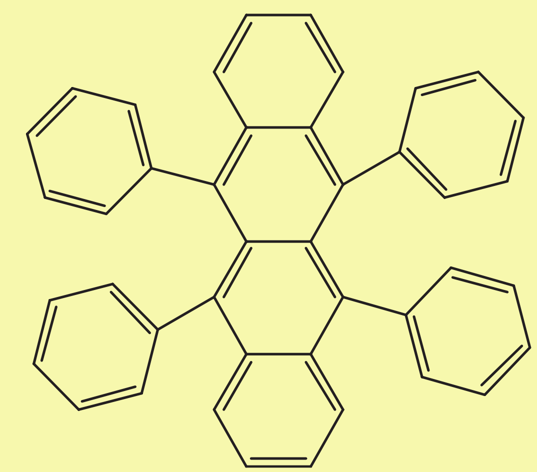
Sensitized Upconversion

Absorption
Sensitizer $PdPQ_4$



M.J. Crossley, Univ. Sidney

Emission
Emitter rubrene

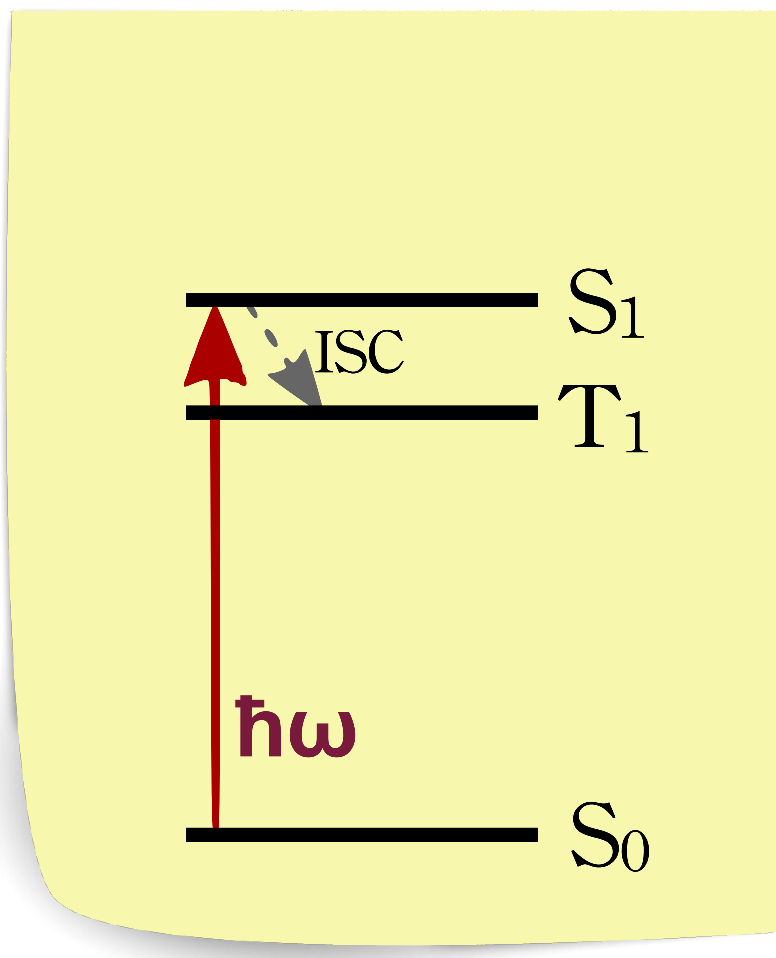


Taima et al., Solar Energy Materials & Solar Cells, 93 (2009)

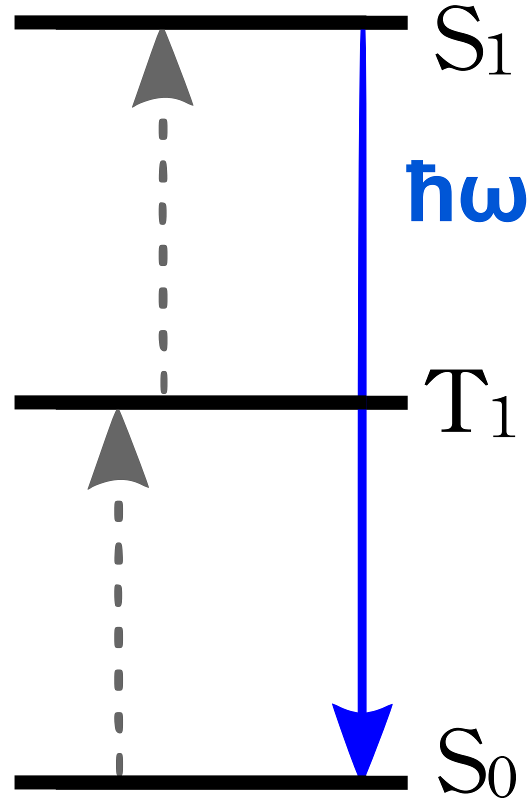
- intra- and intermolecular processes result in upconversion

Other combinations see e.g. Singh-Rachford, Coord. Chem. Rev 254, 2560 (2010)

Sensitized Upconversion



Emitter



Dexter type energy transfer

rate $k \sim \exp(-r)$

→ diffusion controlled

Requirements:

$E(T_1^{(S)}) \gtrapprox E(T_1^{(E)})$

$2\,E(T_1^{(E)}) \approx E(S_1^{(E)})$

Upconversion:

$T_1^{(E)} + T_1^{(E)} \rightarrow S_1^{(E)} \rightarrow h\nu$

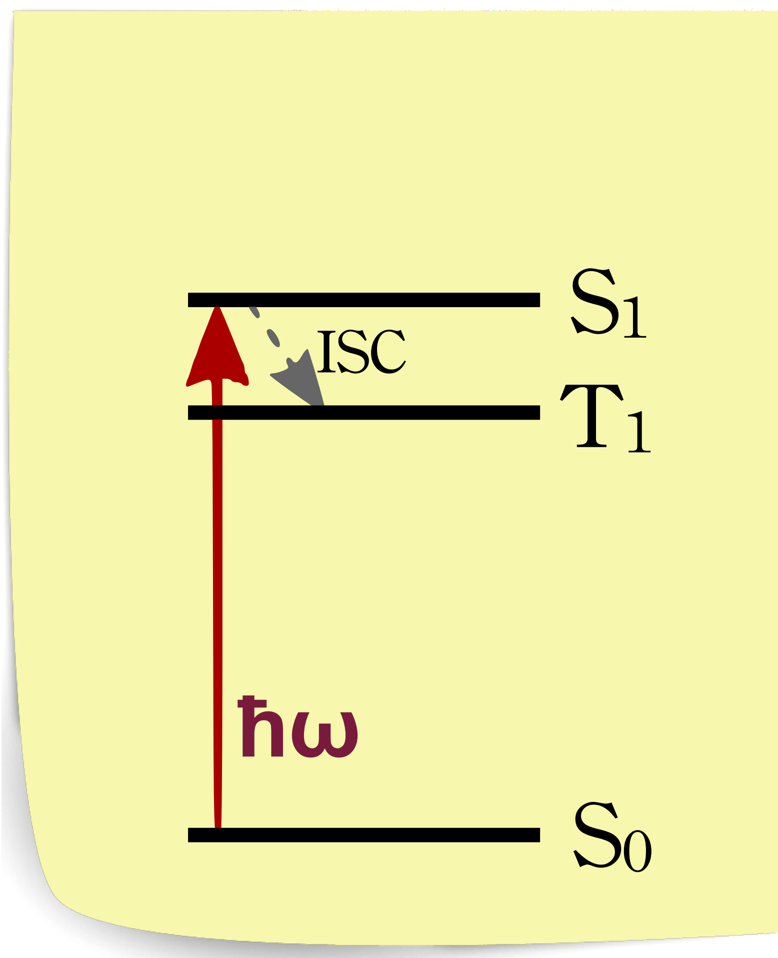
nonradiative transition

spin forbidden
lifetime 100mus, 1ms

inter and intramolecular prcoesses

Sensitized Upconversion

Sensitizer



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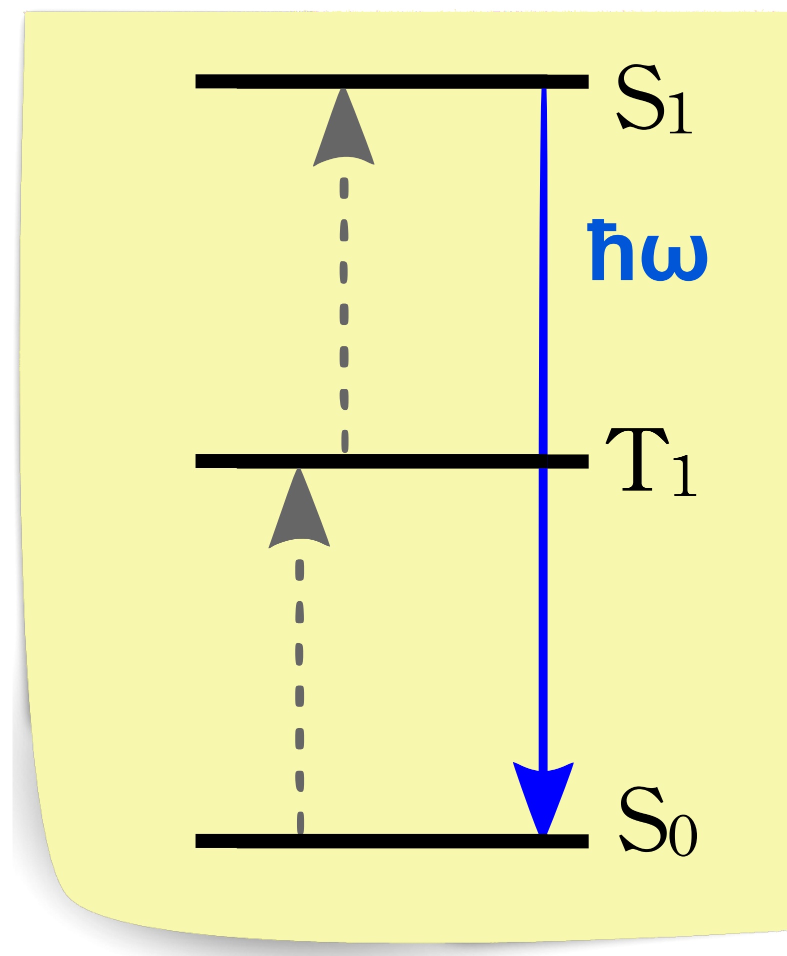

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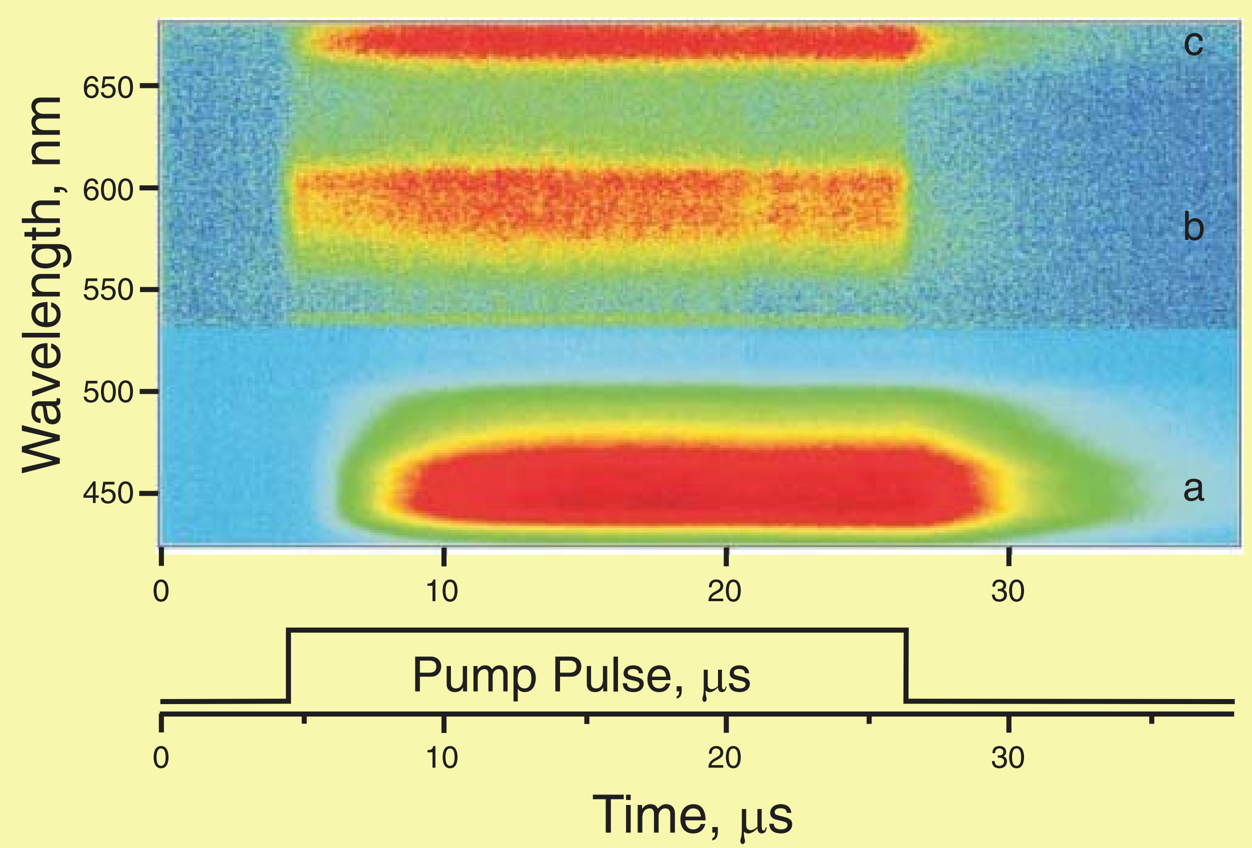
Sensitized Upconversion

- Triplet-Triplet Fusion

  → nonlinear process

- Sunlight suffices

- Efficient: quantum yield up to 23% measured[2]



Baluschev, PRL 97, 143903 (2006)

1 Ji et al., **EJIC** 19, 3183 (2012)
2 de Wild, **Energy Environ. Sci. (2011)**, 4, 4835

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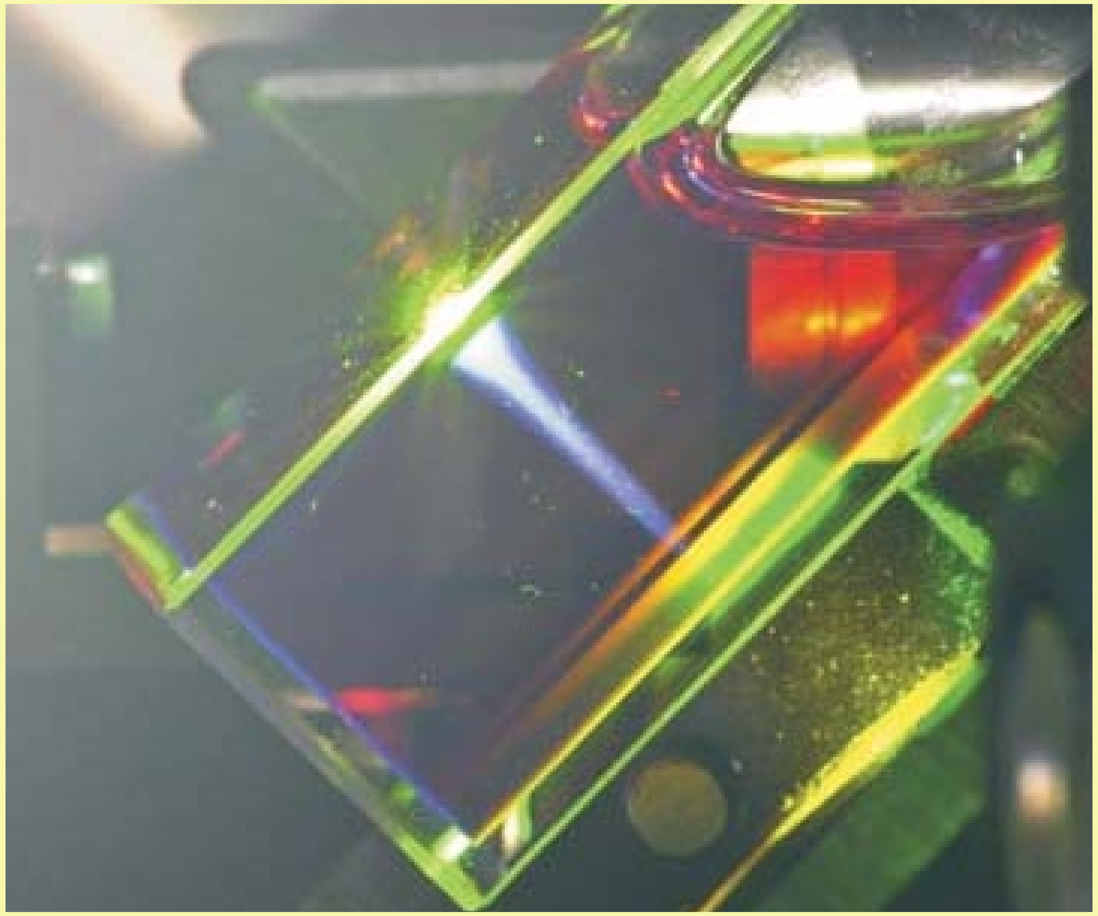

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Standard Theory

$$\partial_t[\mathrm{T}_1^{(S)}] = \Gamma_{\mathrm{ISC}}[\mathrm{S}_1^{(S)}] - \left(\underline{\Gamma_d^{(S)}} + \underline{\Gamma_{(S\to E)}}\right)[\mathrm{T}_1^{(S)}] + \underline{\Gamma_{(E\to S)}}[\mathrm{T}_1^{(E)}]$$

$$\partial_t[\mathrm{T}_1^{(E)}] = \underline{\Gamma_{(S\to E)}}[\mathrm{T}_1^{(S)}] - \left(\underline{\Gamma_d^{(E)}} + \underline{\Gamma_{(E\to S)}}\right)[\mathrm{T}_1^{(E)}] - \underline{\Gamma_{\mathrm{TTA}}[\mathrm{T}_1^{(E)}]^2}$$

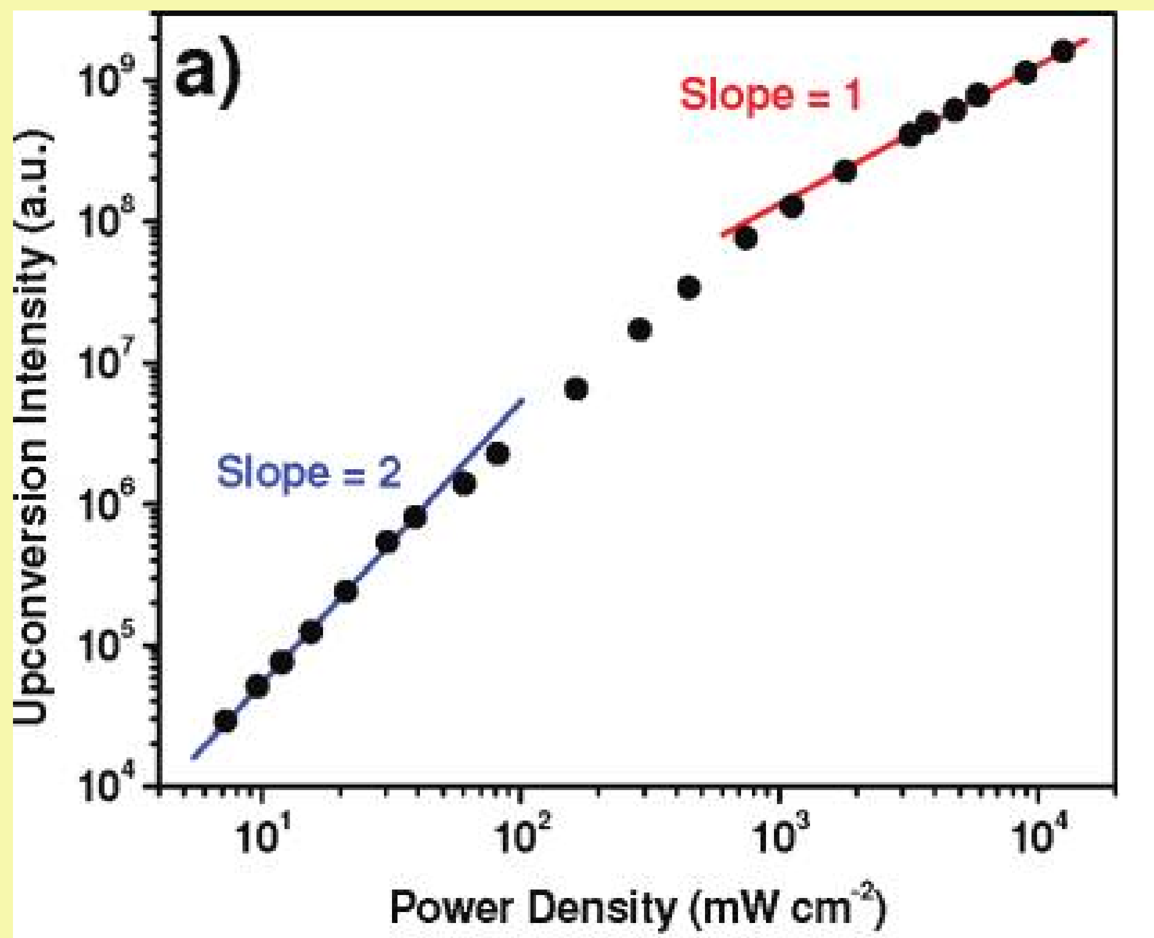
finite lifetime

energy transfer

upconversion

$$\mathrm{I_{UC}} \overset{\mathrm{I_{inc}}\to 0}{\approx} \frac{f y^2}{32\Gamma_{\mathrm{TTA}} x^2} \sim \mathrm{I_{inc}^2}$$

$$\mathrm{I_{UC}} \overset{\mathrm{I_{inc}}\to \infty}{\approx} \frac{f y}{8\Gamma_{\mathrm{TTA}}} \sim \mathrm{I_{inc}}$$

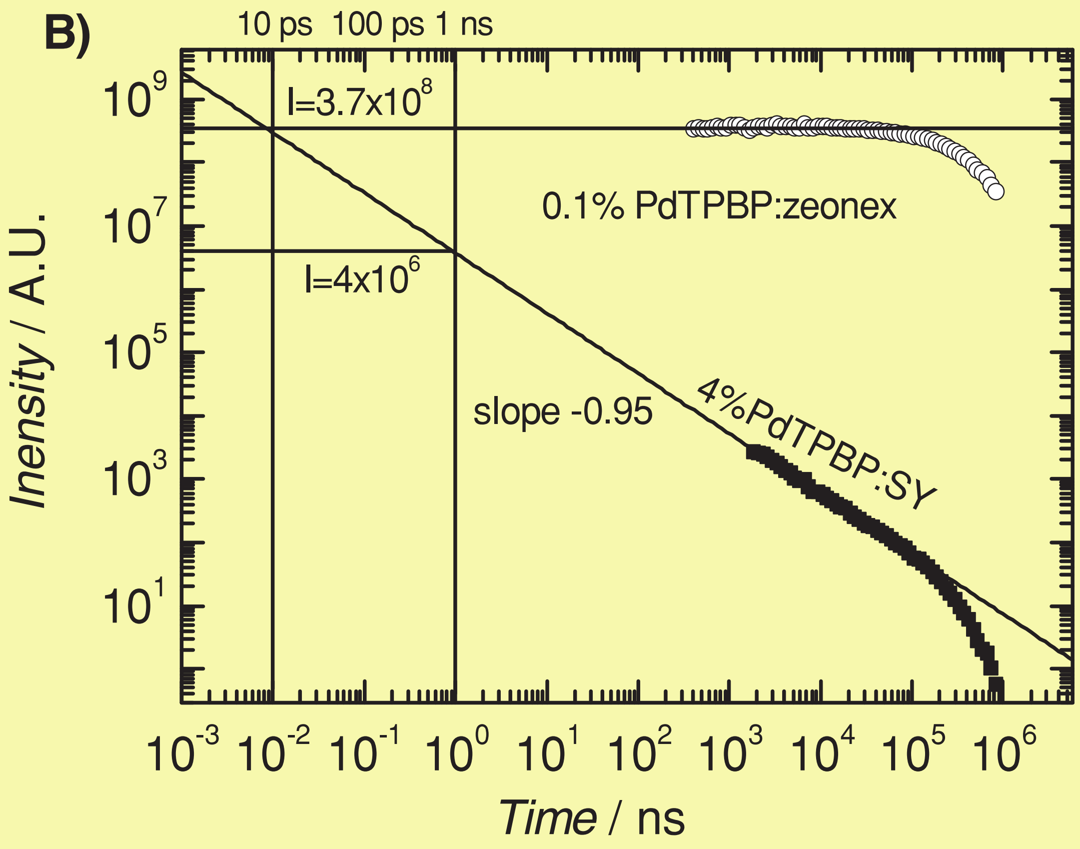


Haefele et al., J. Phys. Chem. Lett. **(2006)** 3, 299

Transient dynamics

$$[\mathrm{T}_1^{(E)}](t) = \left[e^{\Gamma_d^{(E)} t} \left(1/[\mathrm{T}_1^{(E)}](0) + \Gamma_{\mathrm{TTA}}/\Gamma_d^{(E)} \right) - \Gamma_{\mathrm{TTA}}/\Gamma_d^{(E)} \right]^{-1} \quad \sim \quad (\Gamma_{\mathrm{TTA}}\, t)^{-1}$$

theory in agreement
with some experiments



Jankus et al., Adv. Funct. Mater. **(2013)**, 23, 384

Transient dynamics

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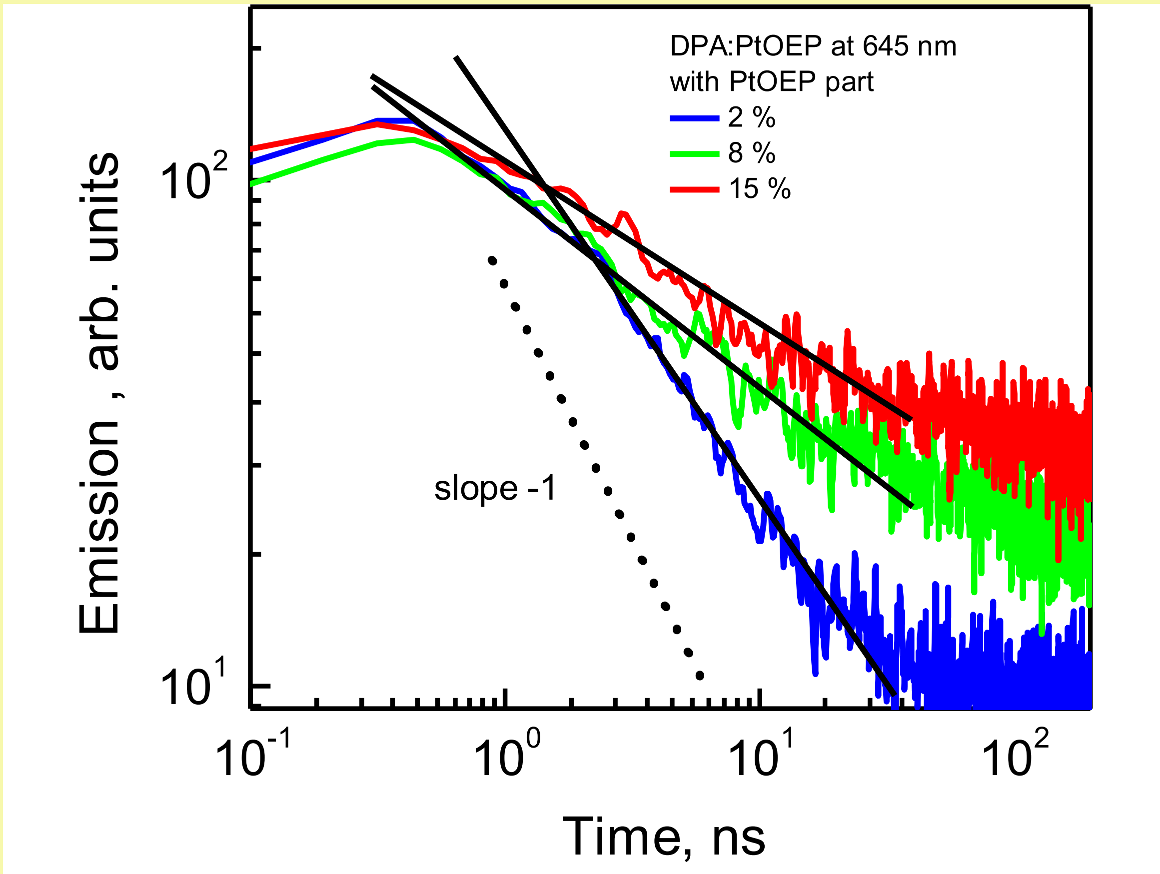
theory in agreement
with some experiments
...
but not with all



Karpicz et al., Chem. Phys. **(2014)**, 429, 57

Fundamental Processes

Energy Transfer:

$T_1^{(E)} + S_0^{(E)} \rightarrow S_0^{(E)} + T_1^{(E)}$

$T_1^{(S)} + S_0^{(S)} \rightarrow S_0^{(S)} + T_1^{(S)}$

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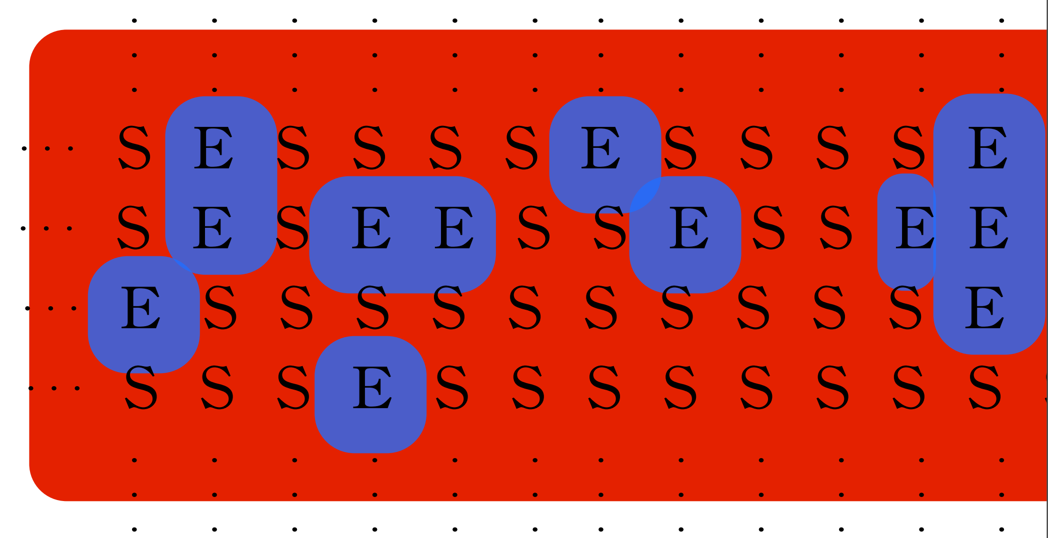

Decay:

$T_1^{(S)} \rightarrow S_0^{(S)}$

$T_1^{(E)} \rightarrow S_0^{(E)}$

Upconversion:

$T_1^{(E)} + T_1^{(E)} \rightarrow S_0^{(E)} + S_1^{(E)} \rightarrow h\nu$

Annihilation:

$T_1^{(S)} + T_1^{(S)} \rightarrow T_1^{(S)} + S_0^{(S)}$

$T_1^{(S)} + T_1^{(E)} \rightarrow ?\ (S_0^{(S)} + S_0^{(E)})$

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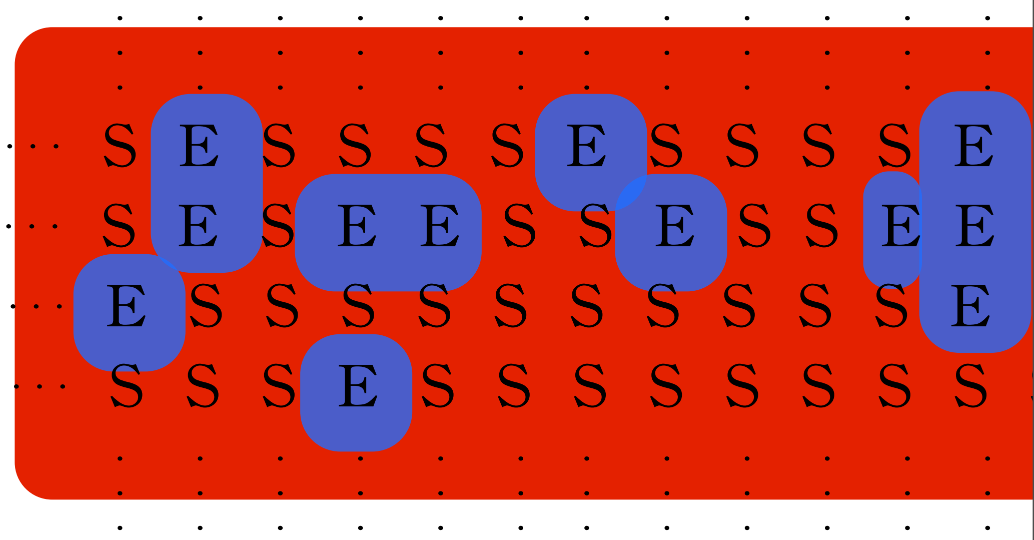
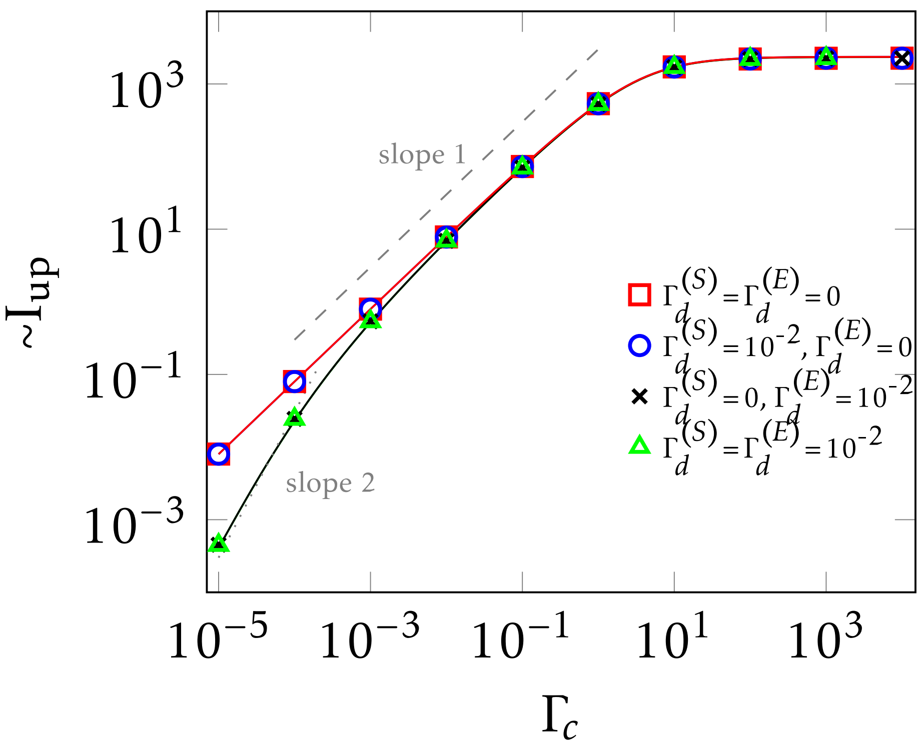
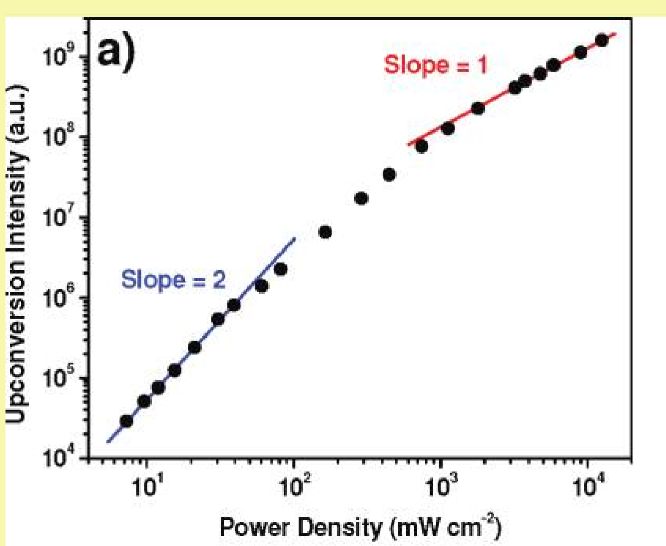


- Random molecular network
- Kinetic Monte Carlo simulation
- E-S ratio as parameter

Simulation Results

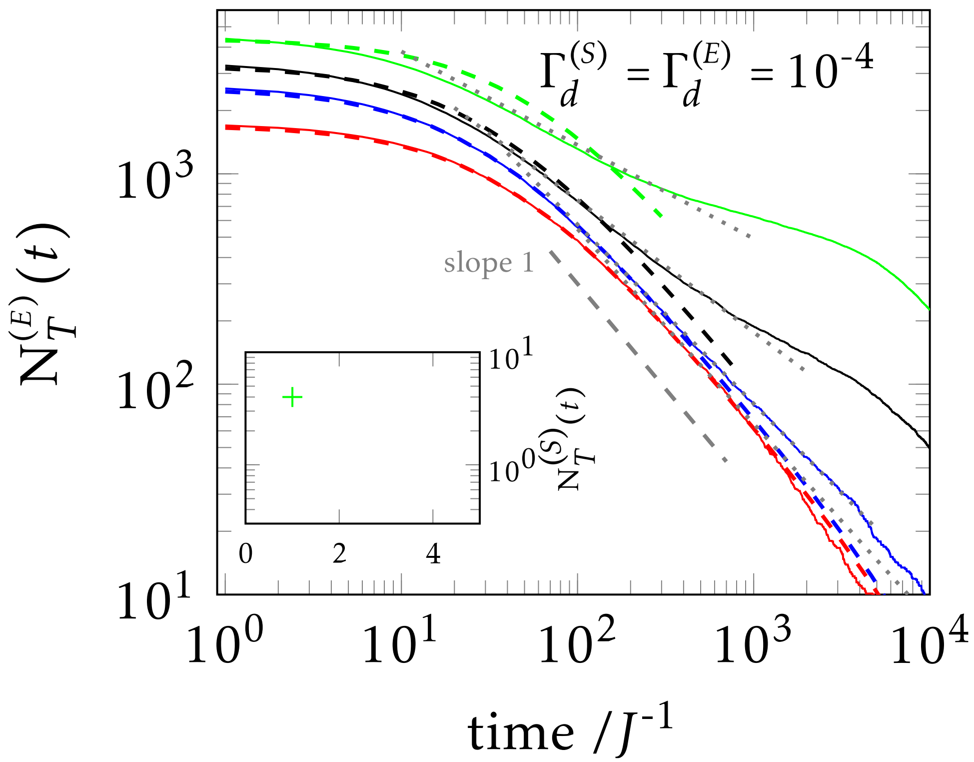
steady state

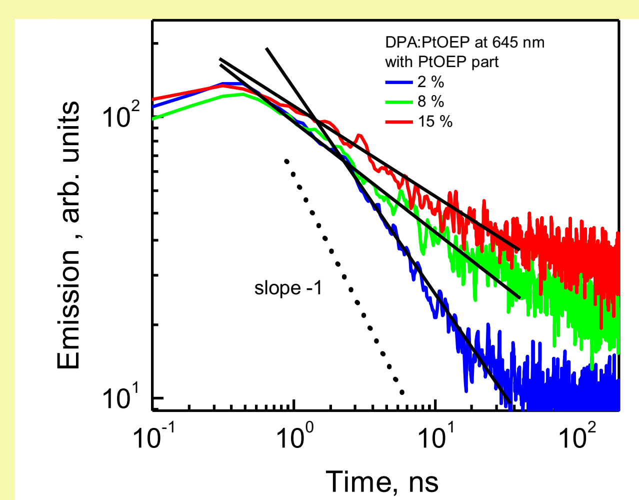




Haefele et al.

transient

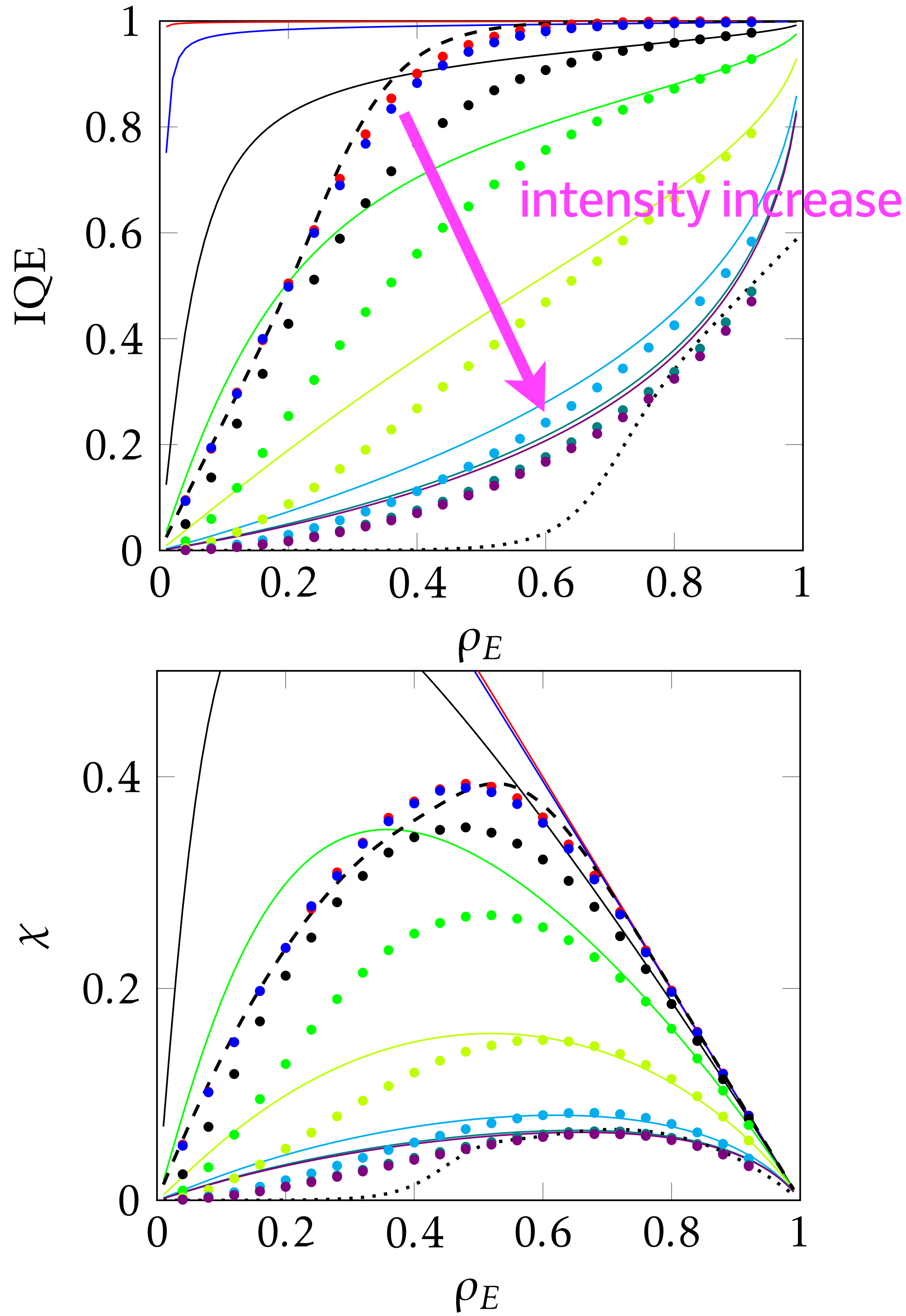




Karpicz et al.

Simulation Results

efficiency



percentage of emitters

efficiency measures

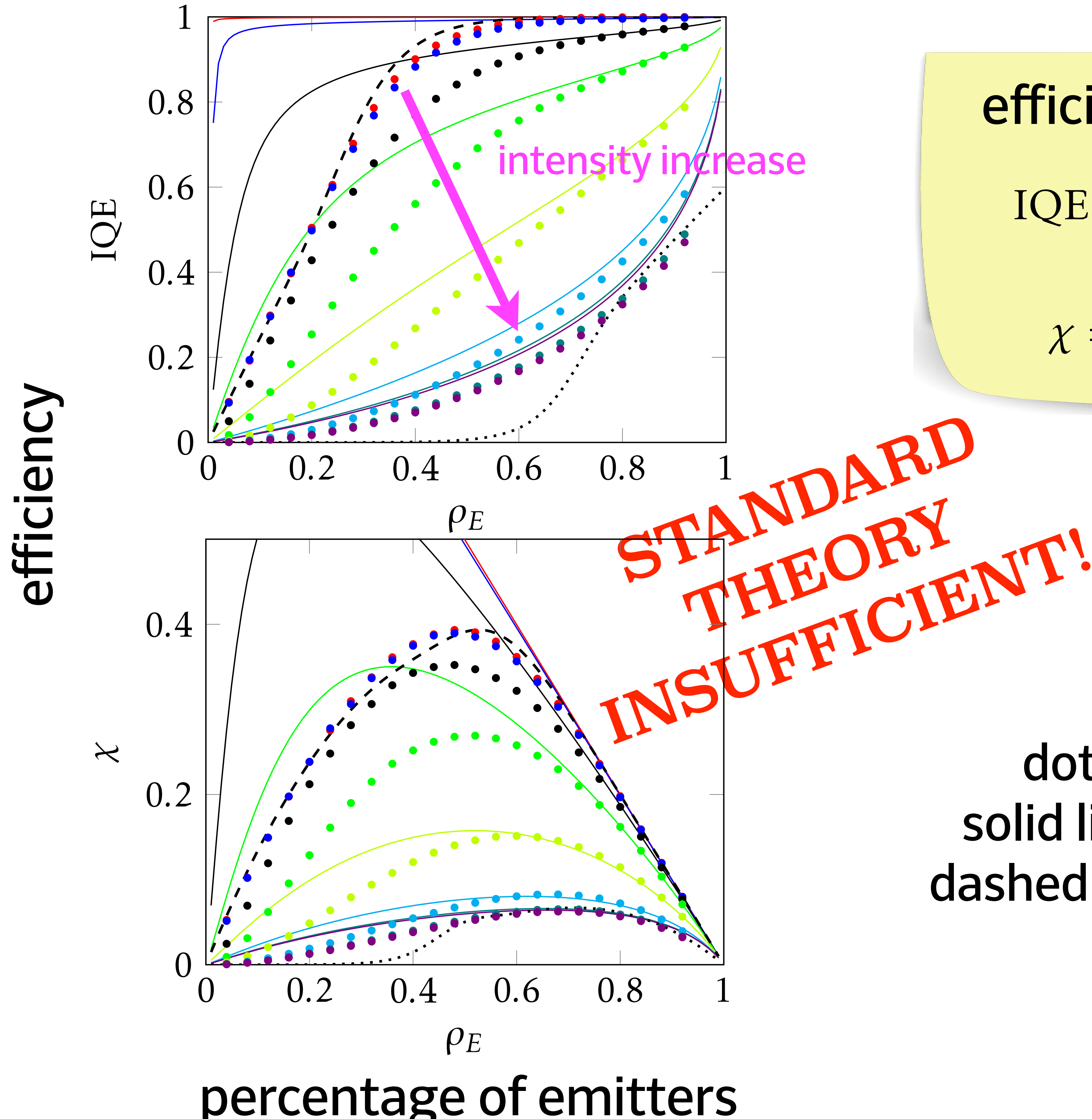
$$\text{IQE} = \frac{\text{no. of upconverted triplets}}{\text{no. of absorbed photons}}$$

$$\chi = (1 - \rho_E)\text{IQE}$$

dots	numerics
solid lines	standard theory
dashed lines	phenom. theory

JZ, PhD thesis **(2015)**, Freidok Uni Freiburg

Simulation Results



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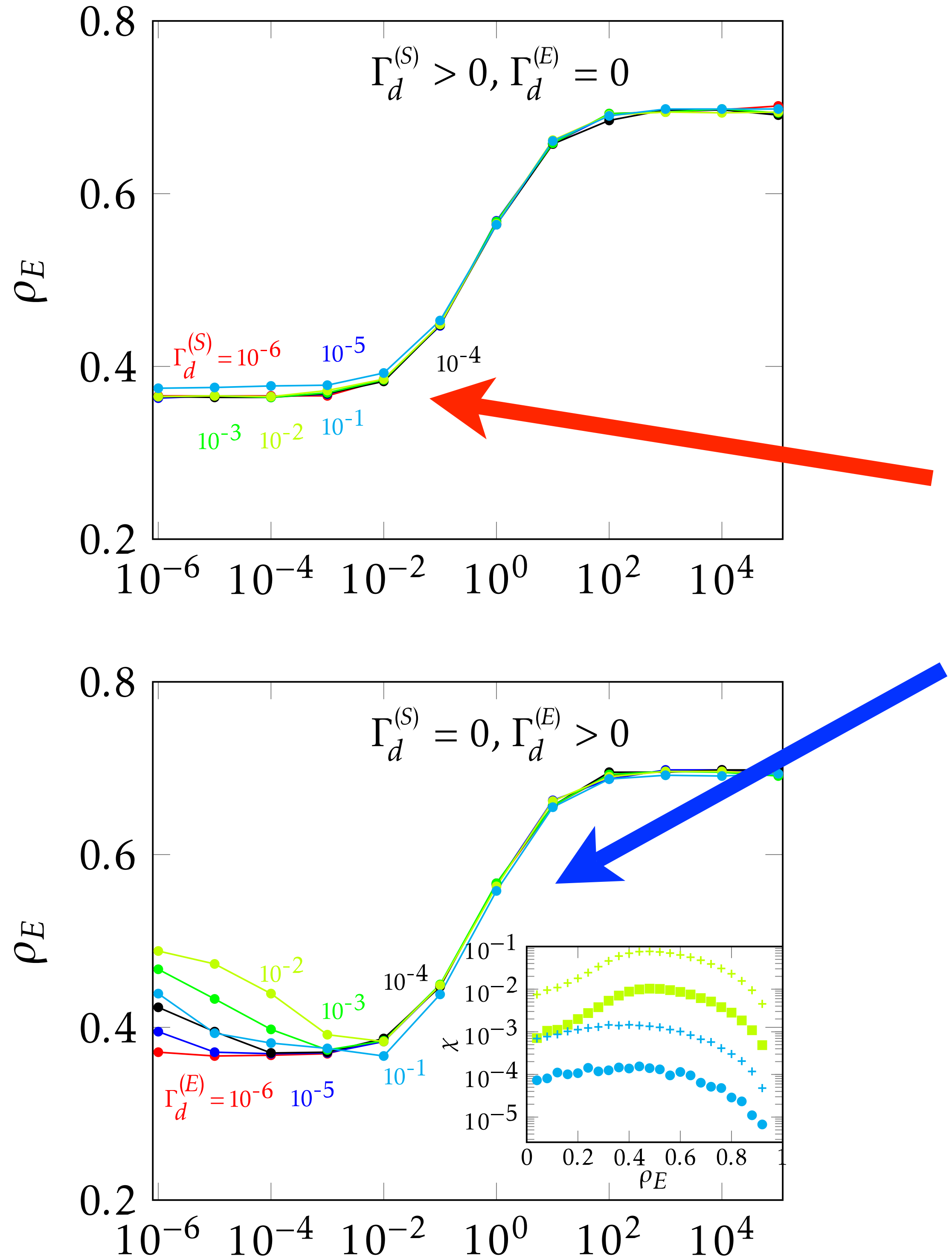
Optimal Structural Parameter

optimal percentage of emitters

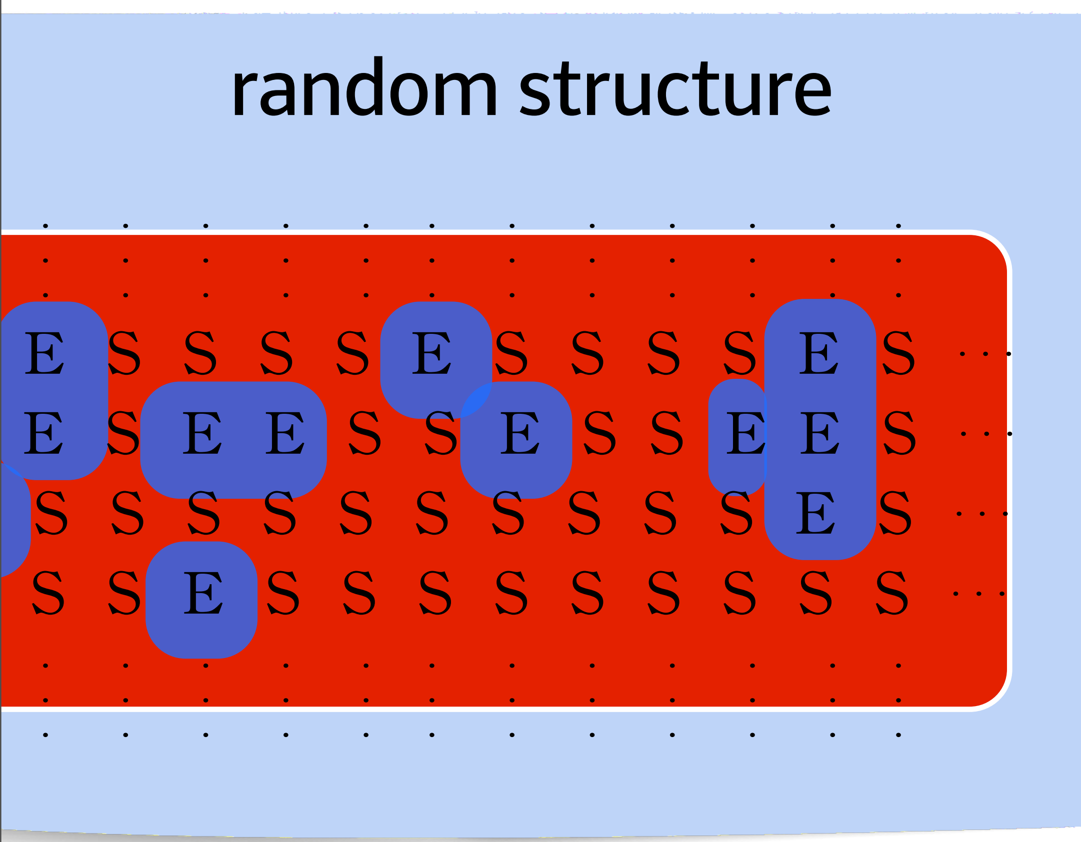


incident light intensity

- step-like dependence on intensity
- no influence of finite sensitizer triplet lifetime
- finite emitter triplet lifetime shifts optimal value

JZ, PhD thesis **(2015)**, Freidok Uni Freiburg

Can we do better?



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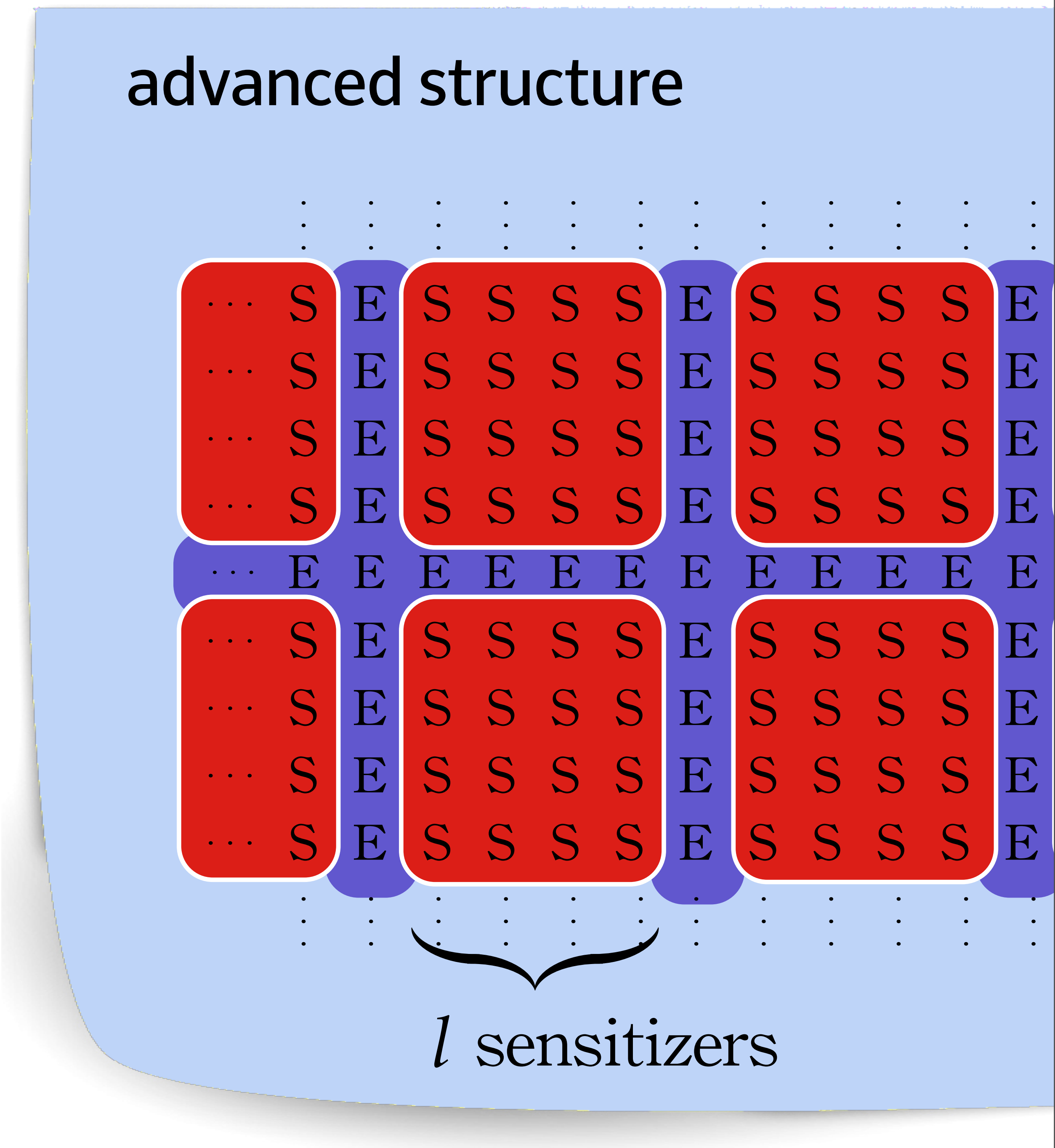
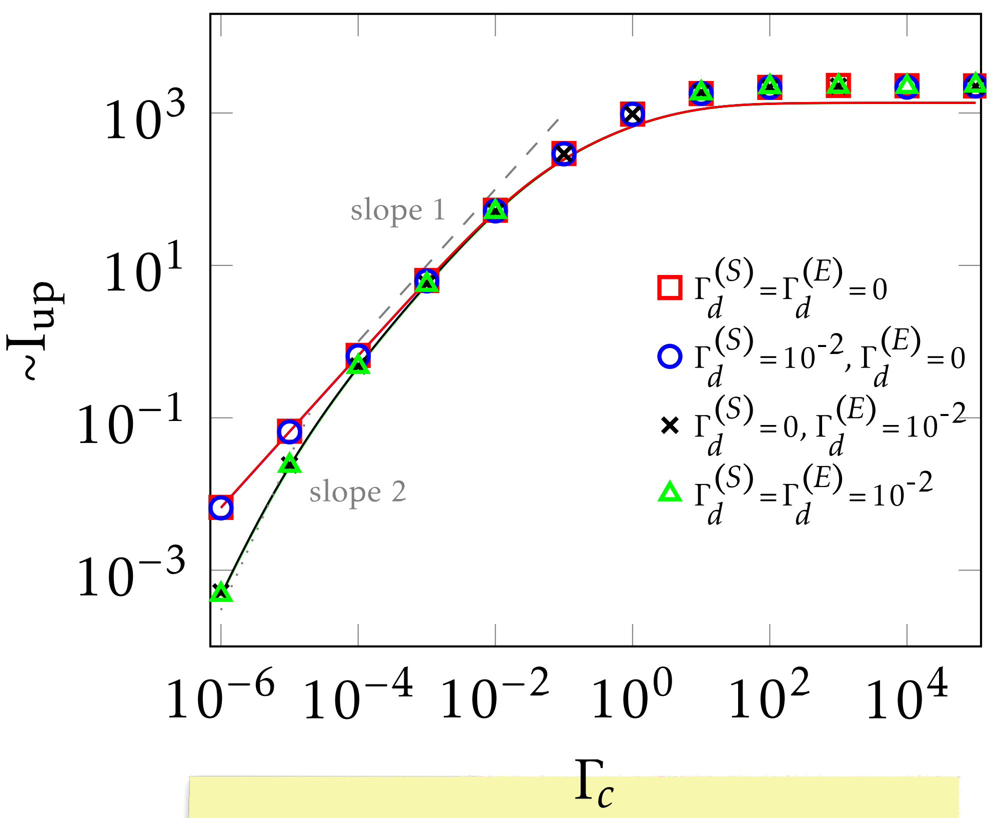
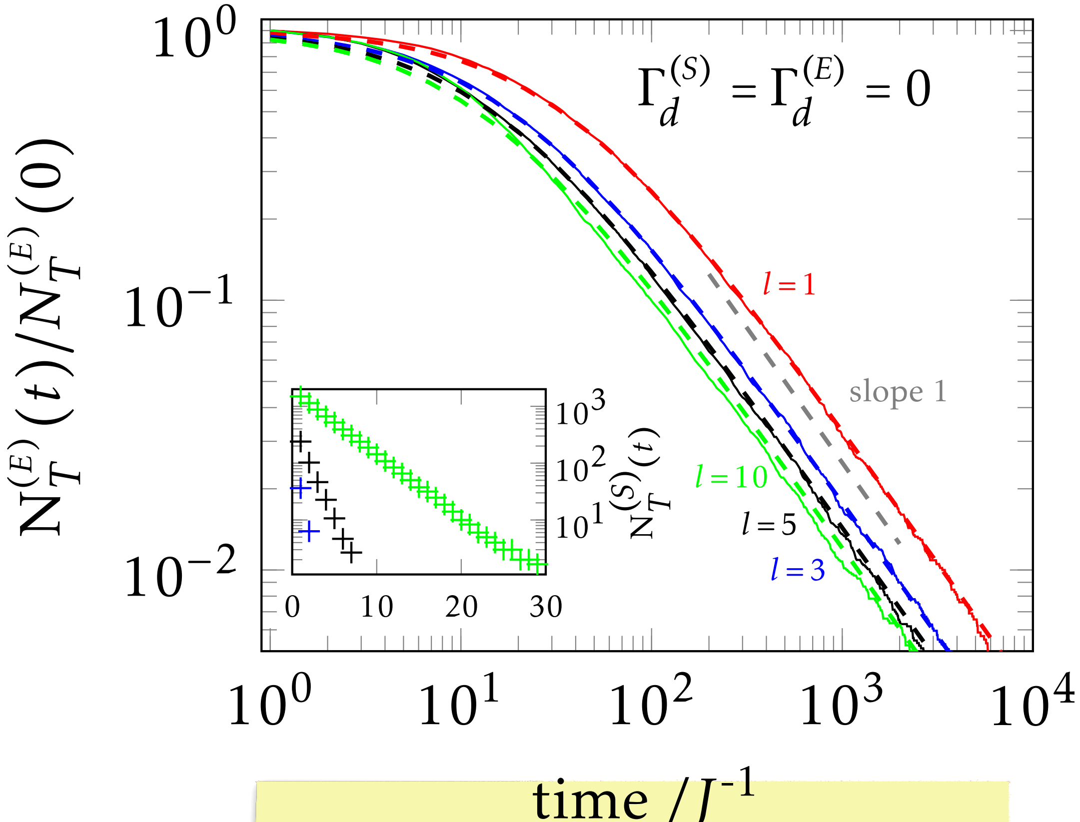


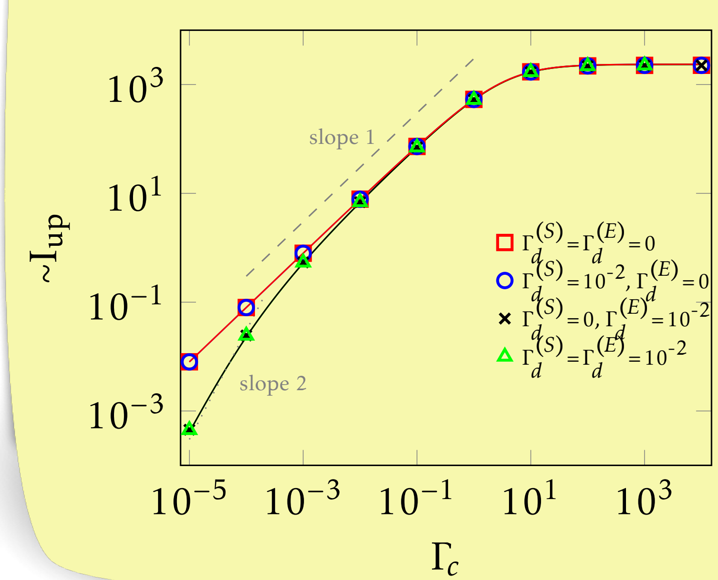
Simulation Results: Advanced Structure

steady state



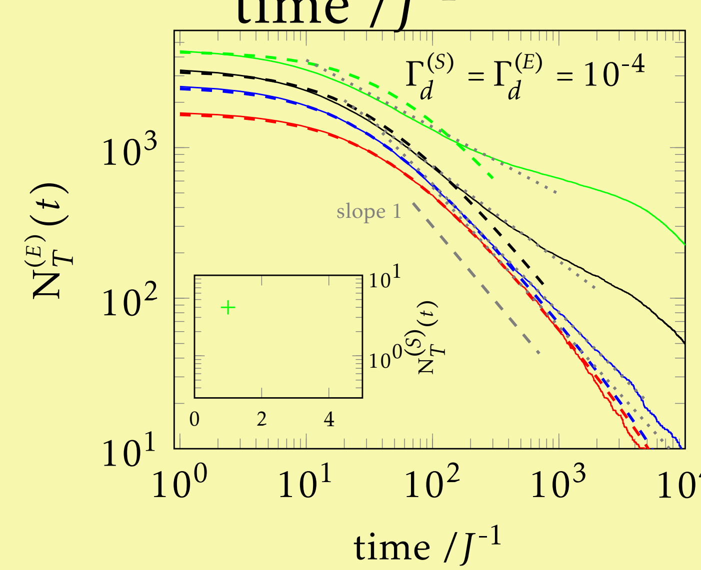
transient





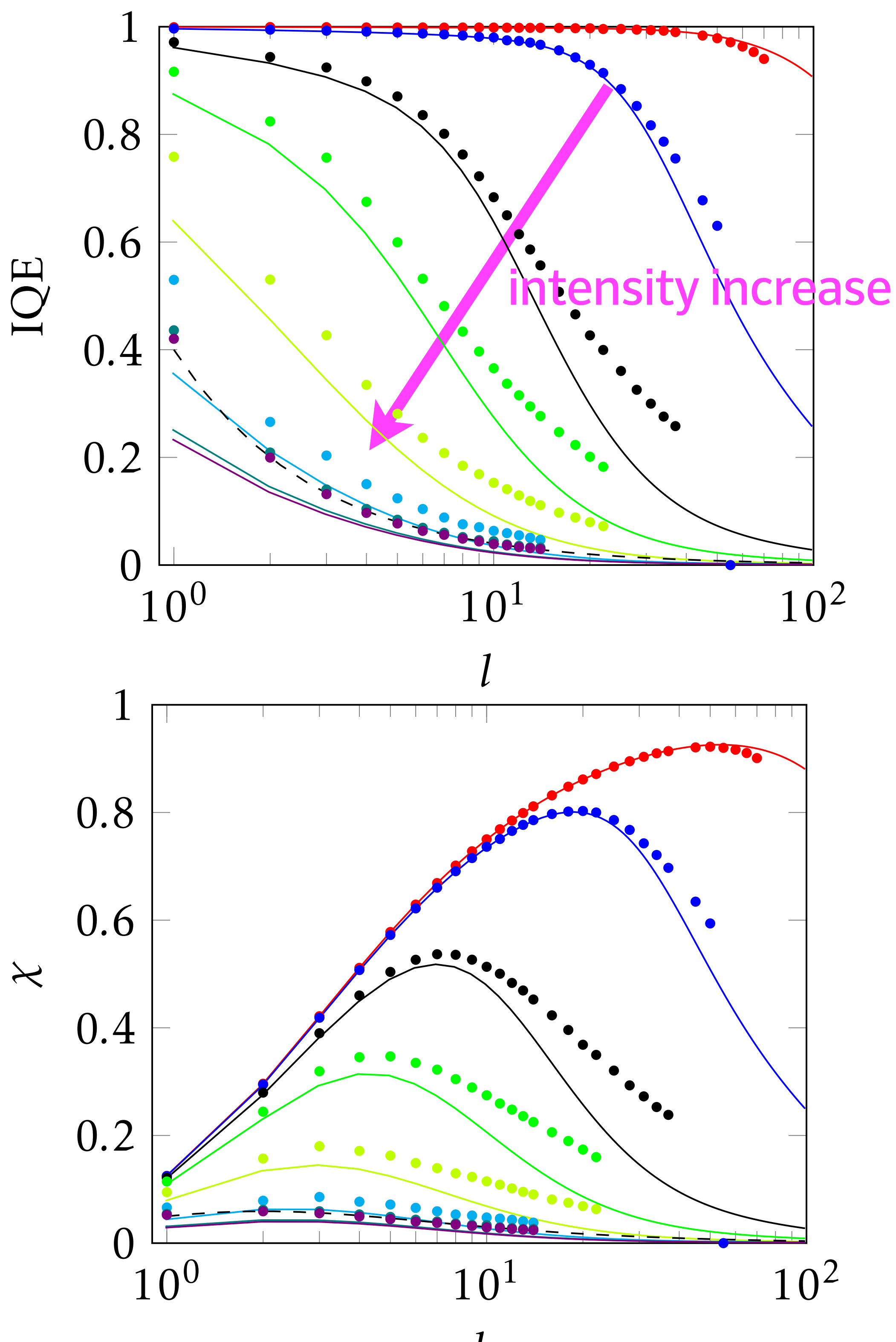
linear onset one order of magnitude earlier

no trapping issues



Simulation Results: Advanced Structure

efficiency



structural parameter

efficiency measures

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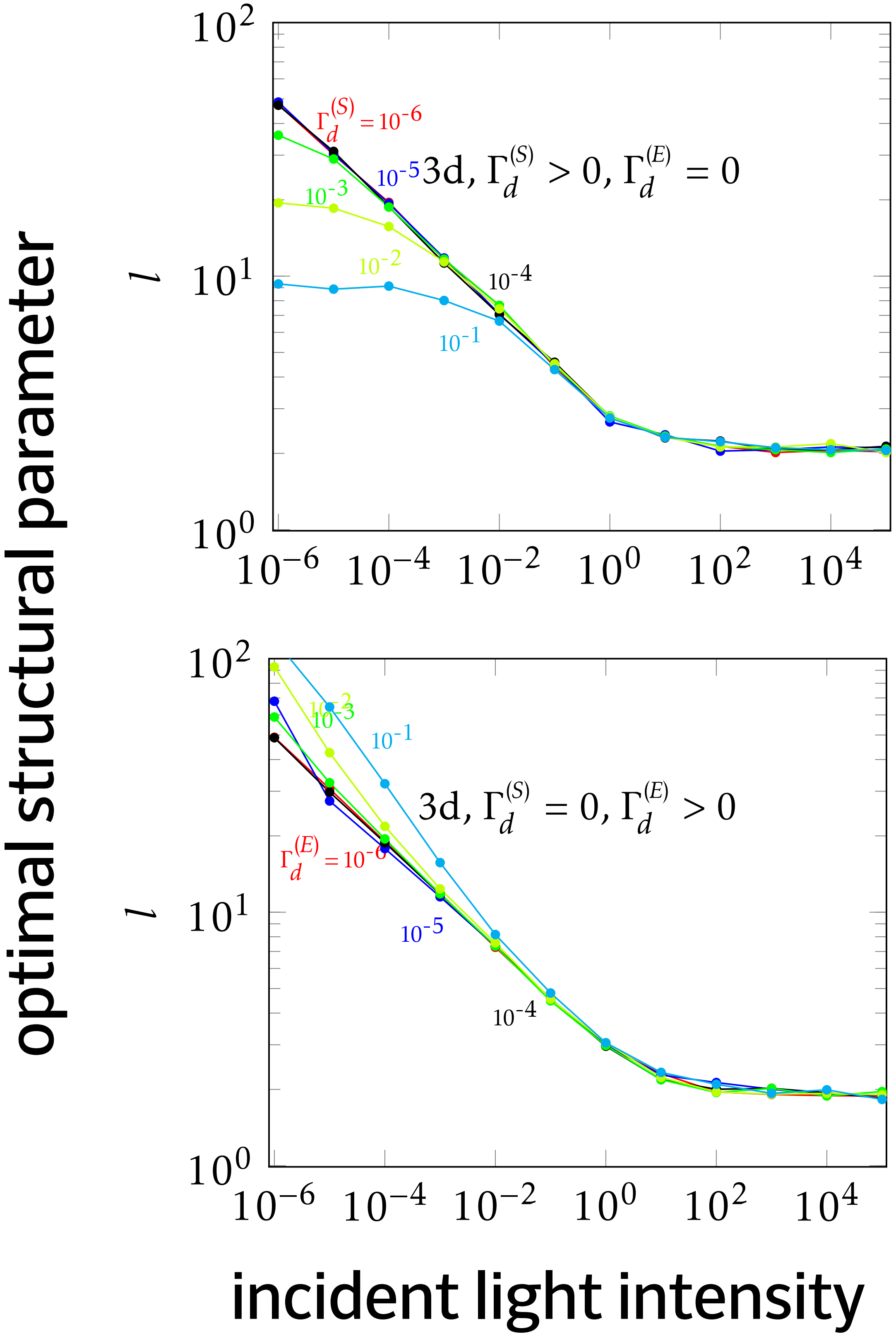
dots	numerics
solid lines	adapted std theory

JZ, PhD thesis **(2015)**, Freidok Uni Freiburg

Optimal Structural Parameter Advanced Structure



- power law dependence on intensity

$$l \sim \left(\frac{J}{\Gamma_c}\right)^{1/5}$$

- finite triplet lifetime shifts optimal value according to a power law

$$l \sim \left(\frac{J}{\Gamma_d^{(S)}}\right)^{1/3} \qquad l \sim \left(\frac{\Gamma_d^{(E)} J}{\Gamma_c^2}\right)^{1/7}$$

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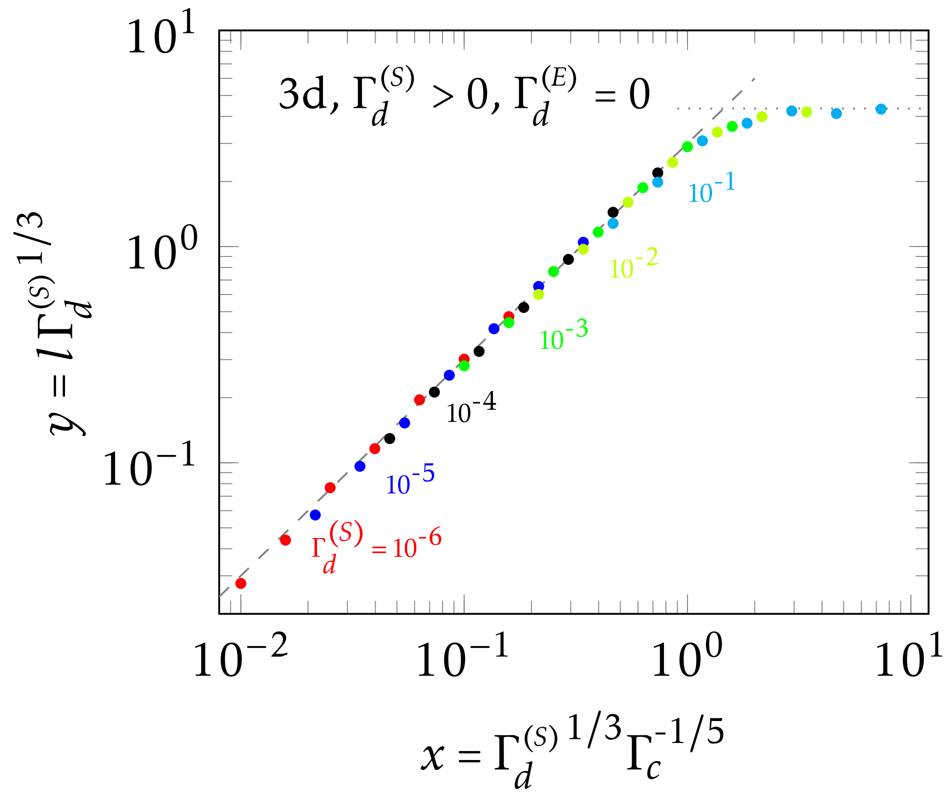
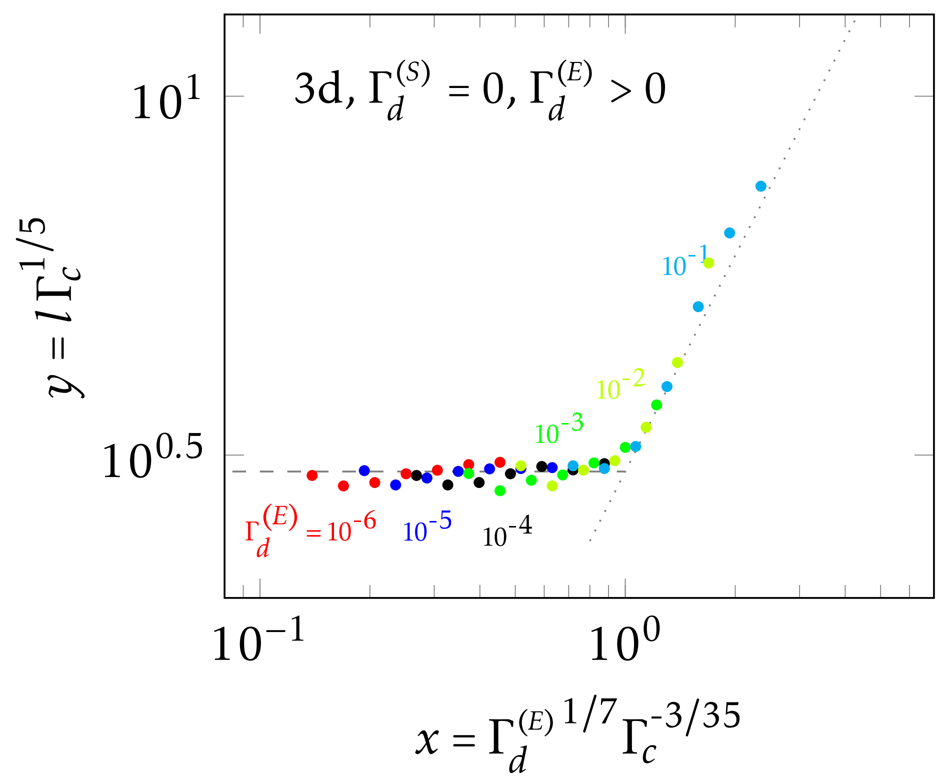
Optimal Advanced Structure: Scaling Laws





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- on rescaled axis all data points collapse to a single curve!

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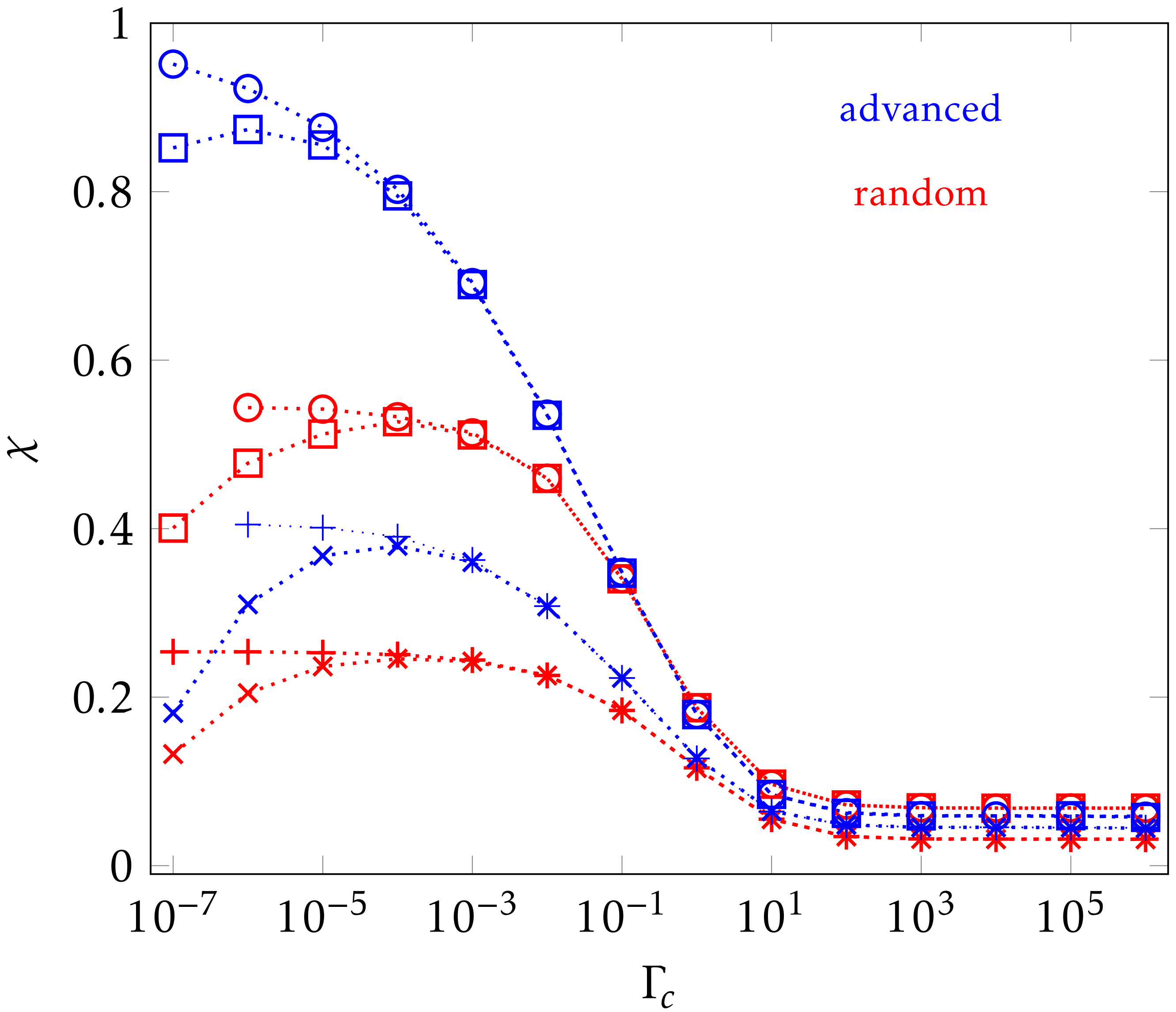
Random vs advanced structure

efficiency for optimal structural parameter



incident light intensity

- advanced structure up to x2 more efficient!

JZ, PhD thesis **(2015)**, Freidok Uni Freiburg
JZ et al., J. Chem. Phys. **(2014)**, 141, 184104

Summary

- Upconversion promising mechanism for light harvesting applications
- Structural optimization improves upconversion efficiency
- Scaling laws reveal universal behavior
- Know optimal emitter ratio as function of material and experimental parameters

JZ, PhD thesis **(2015)**, Freidok Uni Freiburg
JZ et al., J. Chem. Phys. **(2014)**, 141, 184104