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Workshop on Nanoscience for Solar Energy Conversion

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Charge Photogeneration and Collection in Dye Sensitized Solar Cells

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Charge photogeneration and collection in dye sensitised solar cells

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Where do losses in current originate?

$$IPCE(\lambda) = \frac{J_{sc}(\lambda)}{e\Phi(\lambda)} = \eta_{LH}(\lambda)\,\eta_{inj}(\lambda)\,\eta_{coll}(\lambda)$$

short circuit current · *wavelength* · *IPCE* · *elementary charge* · *photon flux* · *light harvesting efficiency* · *injection efficiency* · *collection efficiency*

Spectral Characteristics of Light Harvesting, Electron Injection, and Steady-State Charge Collection in Pressed TiO_2 Dye Solar Cells

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Theoretical Models for the Action Spectrum and the Current–Voltage Characteristics of Microporous Semiconductor Films in Photoelectrochemical Cells

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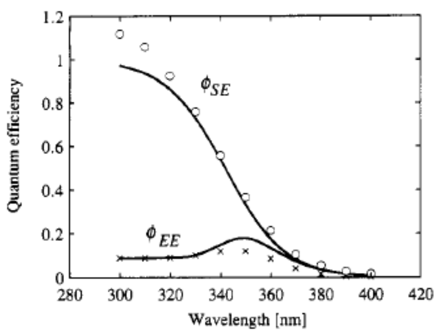
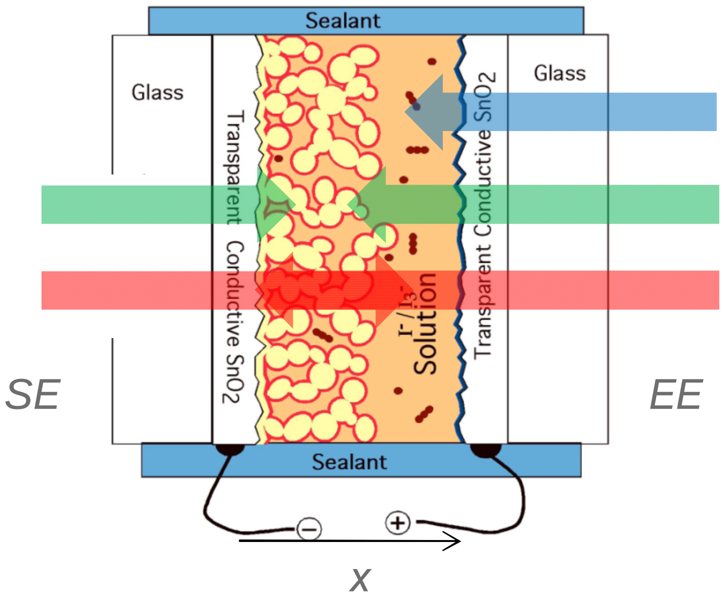
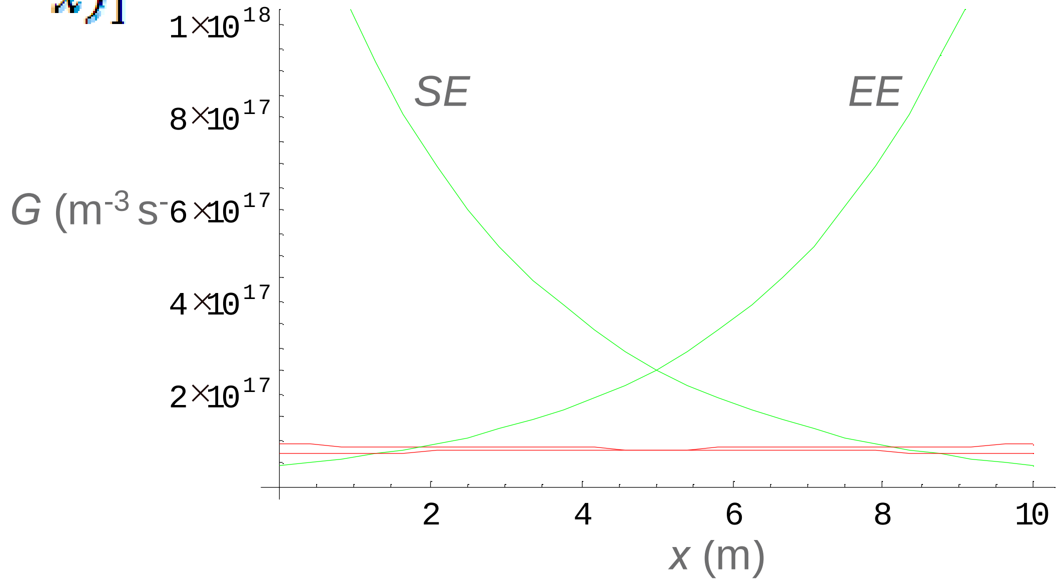


Diffusion length at J_{sc} from 'front' and 'back' IPCE

$$G(x) = \alpha I_0 \exp[-(\alpha + \alpha_i)(d - x)]$$



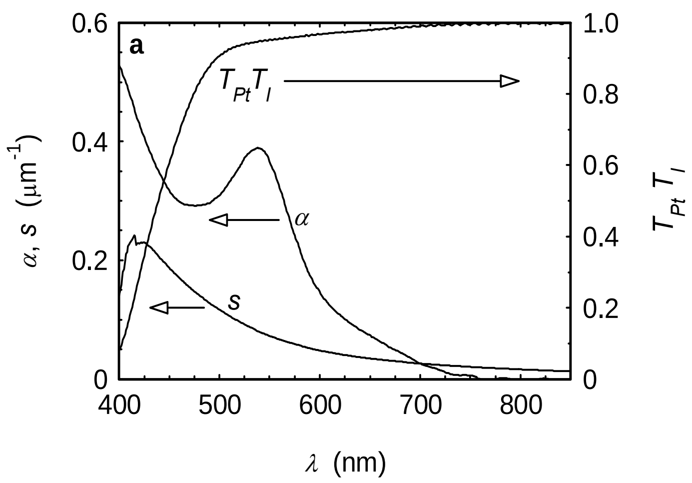


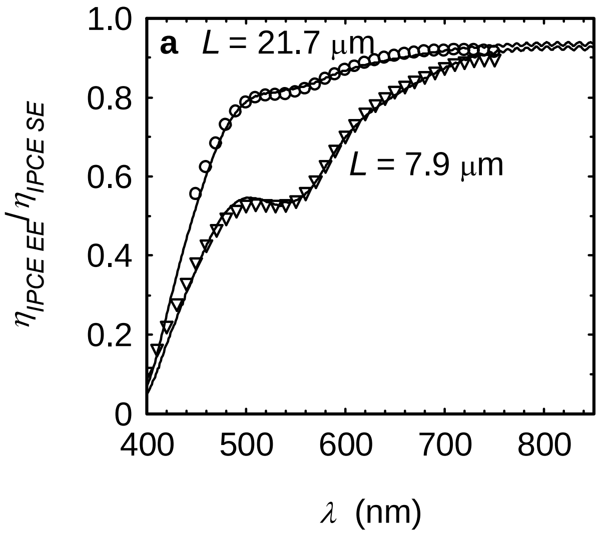
Assuming only 'conducting' electrons are mobile and can recombine

$$\frac{\partial n}{\partial t} = 0 = \eta_{inj} G(x) + D_0 \frac{\partial^2 n_c}{\partial x^2} - \frac{(n_c - n_{eq})}{\tau_0} \quad \textit{at steady state}$$

η_{inj} assumed independent of λ and also E_F for N719

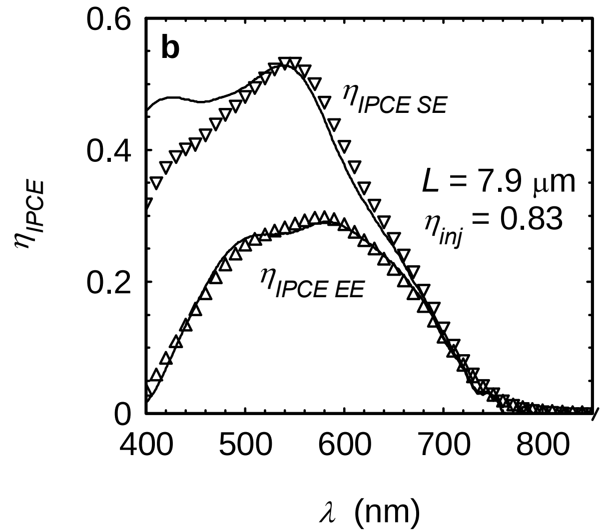
Determining L by fitting to IPCE data





1 free parameter, L

Independent of calibration error

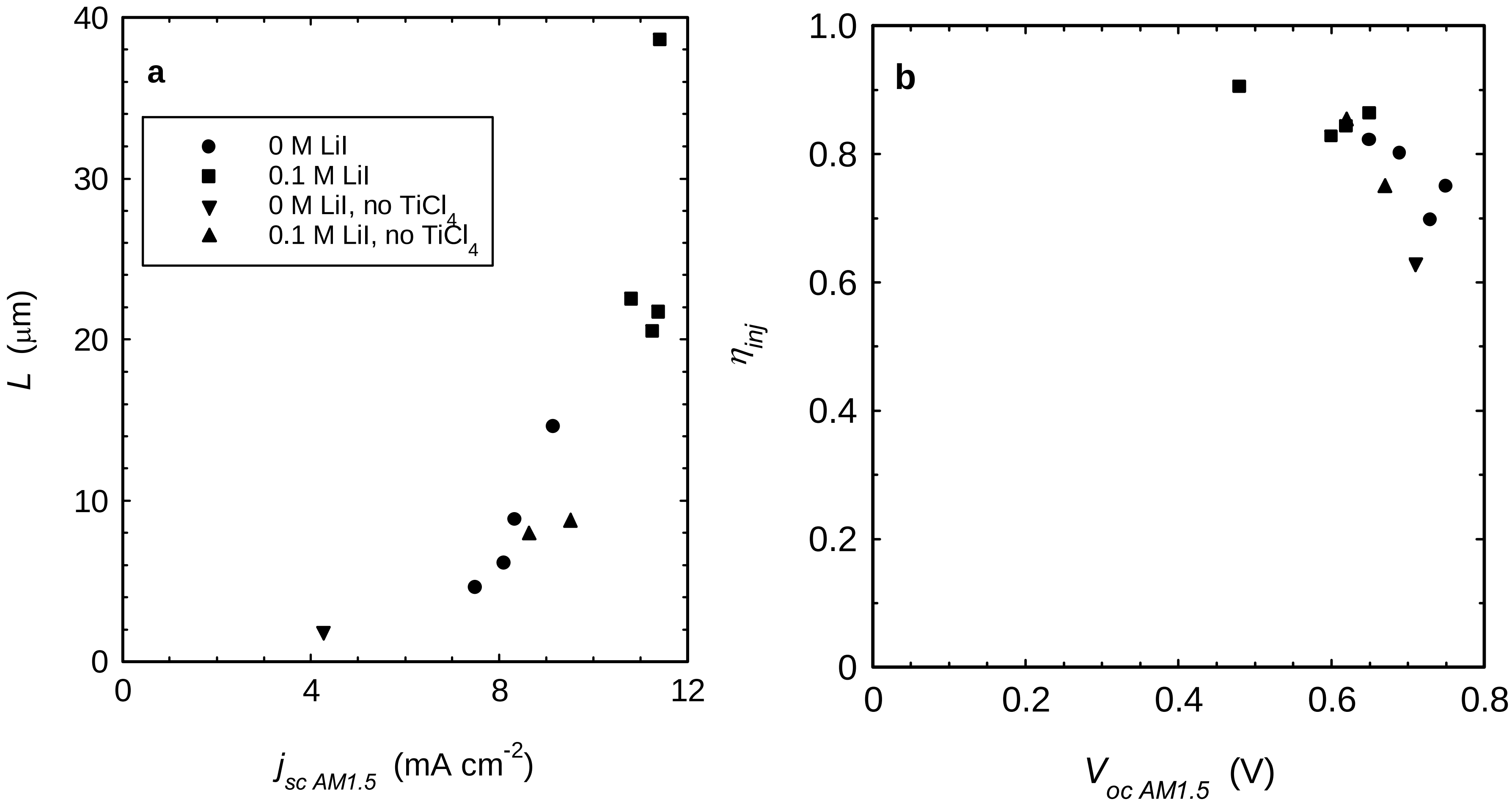


2 free parameters L and η_{inj}

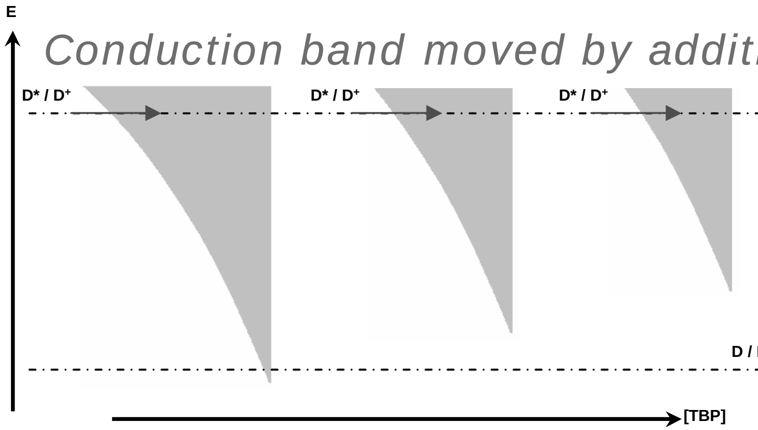
Use L from above, 1 free parameter

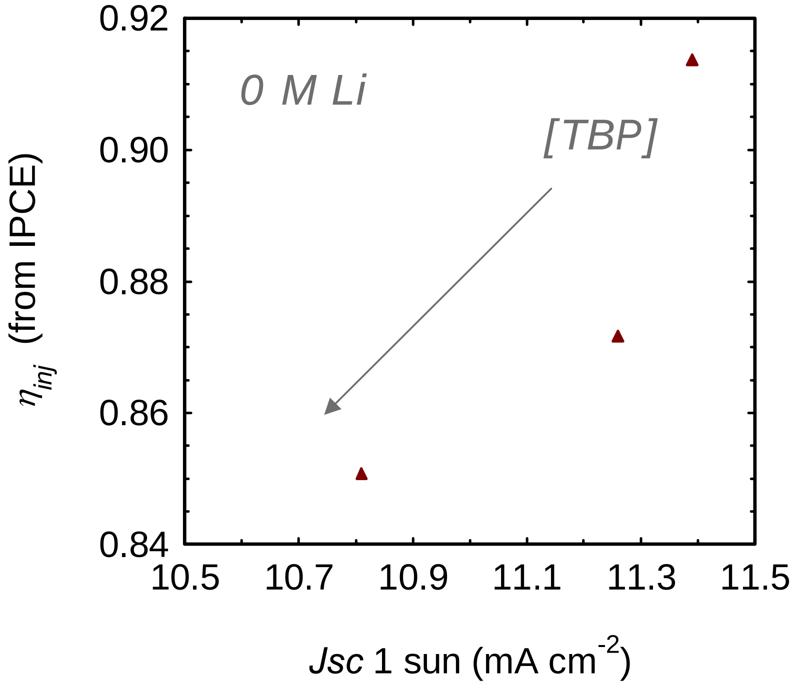
- Measure cell and film thickness
- Measure optical absorption of dyed film, electrolyte and cell
- Measure IPCE from ‘front’ (SE) and ‘back’ (EE)
- Fit expression for EE/SE IPCE → L
- Fit expression to IPCEs → η_{inj}

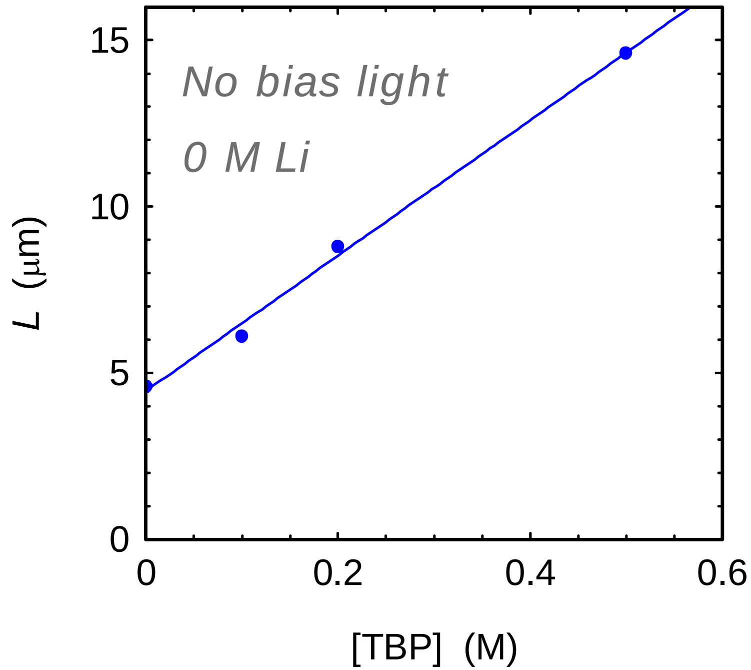
Relationship between fit parameters and IV characteristics



The influence of electrolyte composition

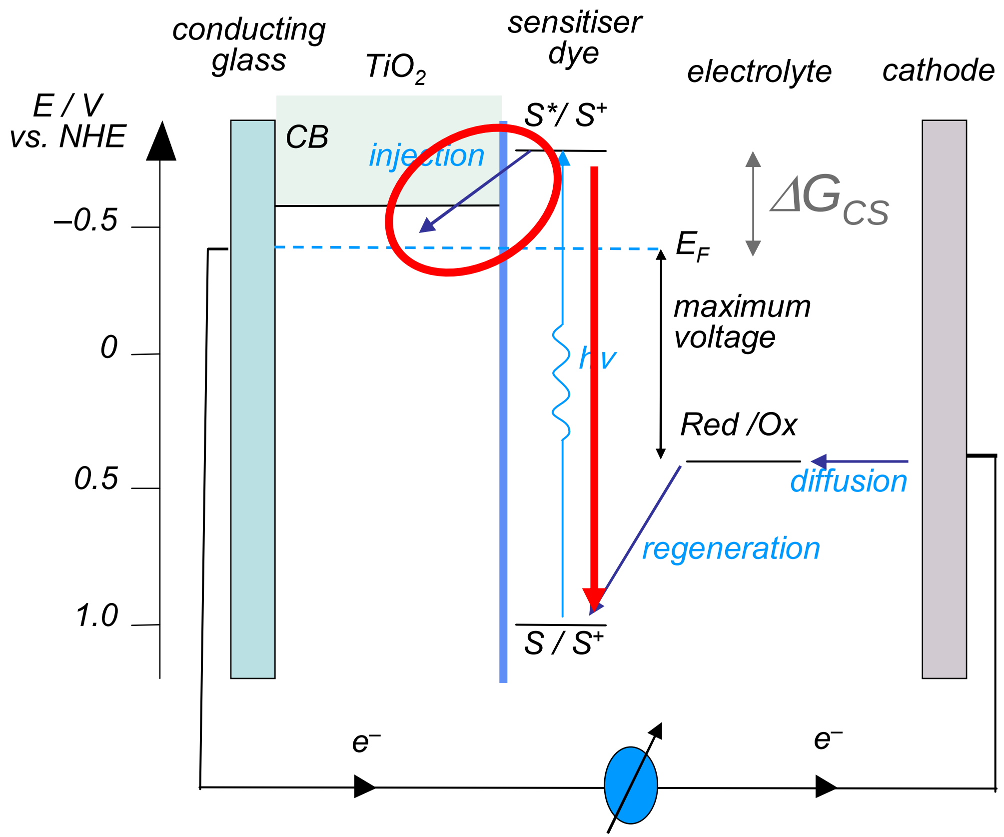






May indicate trap mediated recombination or an interaction between electrolyte and injected carriers at low charge concentrations

Energetics of charge separation: Electron injection

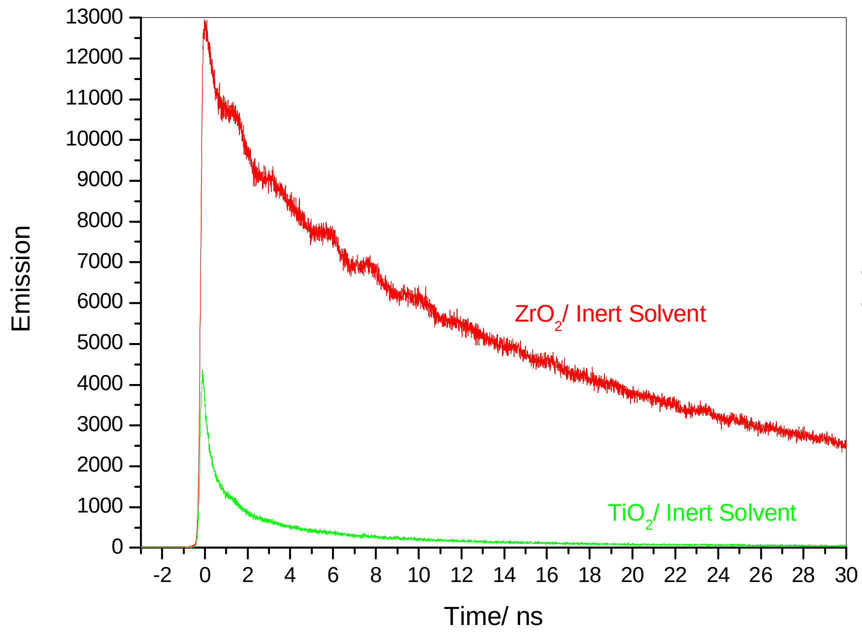


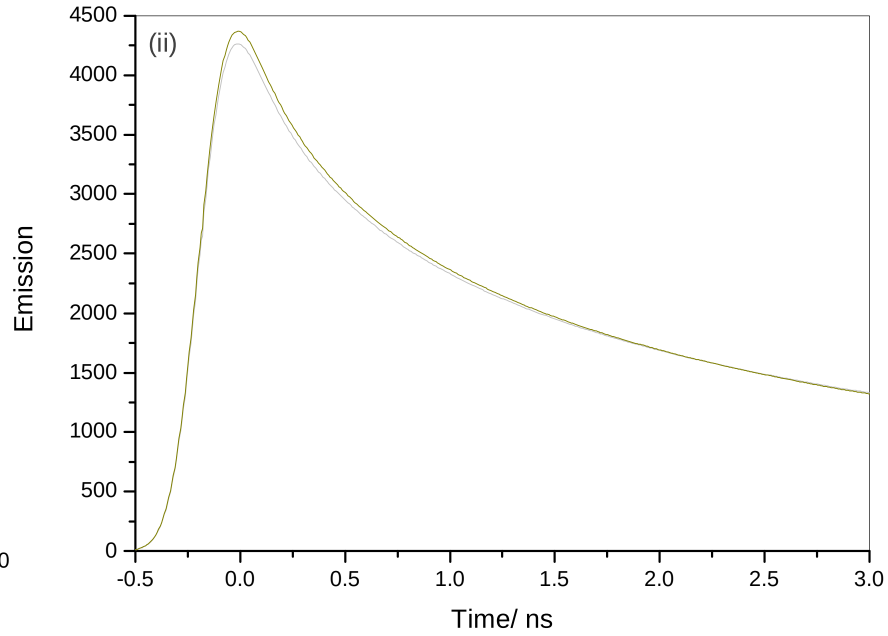
- Dye* → Dye$^+$ + TiO_2(e$^-$)
- Kinetics dependent upon:
  - Electronic coupling
  - Energetics
- Can occur on femtosecond timescales if coupling and energetics sufficiently favourable.
- Efficient device performance only requires injection to be fast compared to excited state decay to ground

For most 'optimised' DSSCs, injection efficiency is a key limitation on device performance

Single Photon Counting – injection efficiency

Identical cells fabricated using injecting and non injecting substrates (titania or zirconia) – emission quenched by injection





Emission decays fit using a stretched exponential convolved with instrument response function → $t_{1/2}$ and η_{inj}

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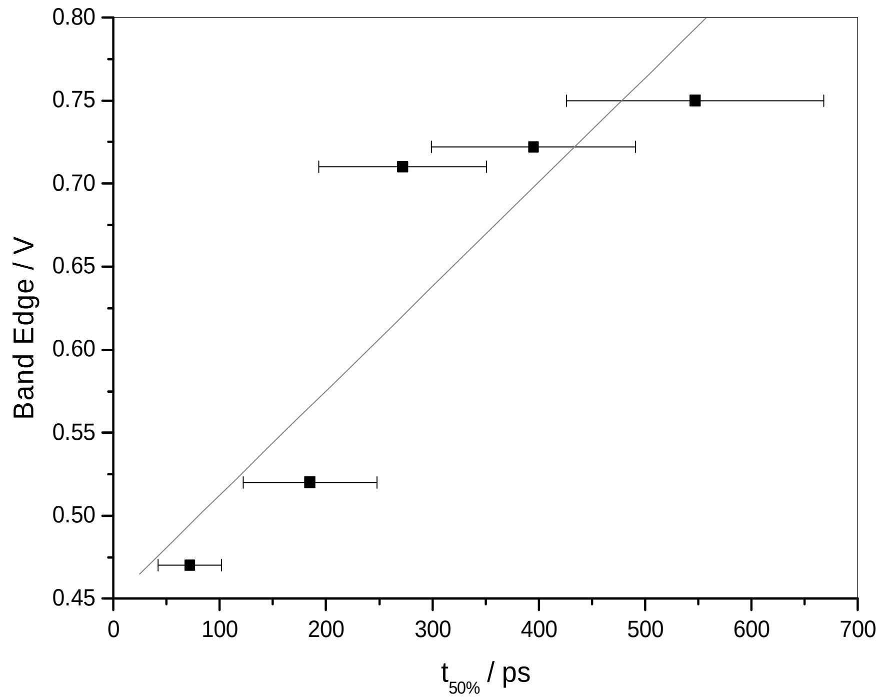
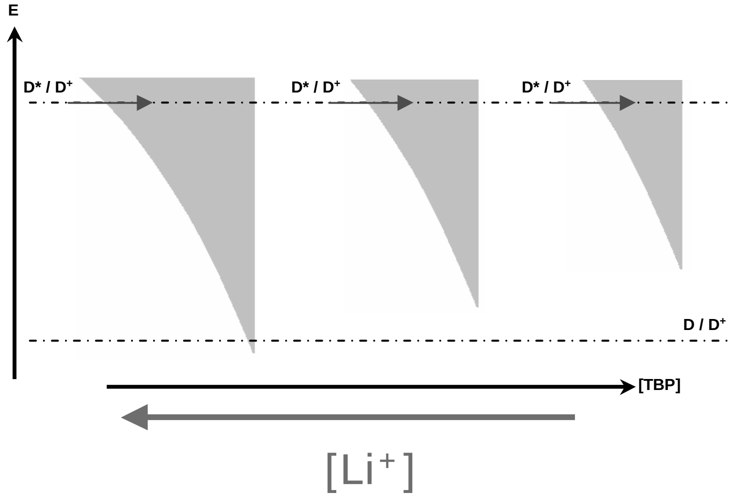
Injection speed - Single Photon Counting



Injection can be slow if conduction band pushed high enough



300 meV shift in CB results in ~ 10 fold retardation of injection

$k_{inj} \propto DOS_{cb} \propto exp(E/E_0)$, E_0 ~100-150 meV

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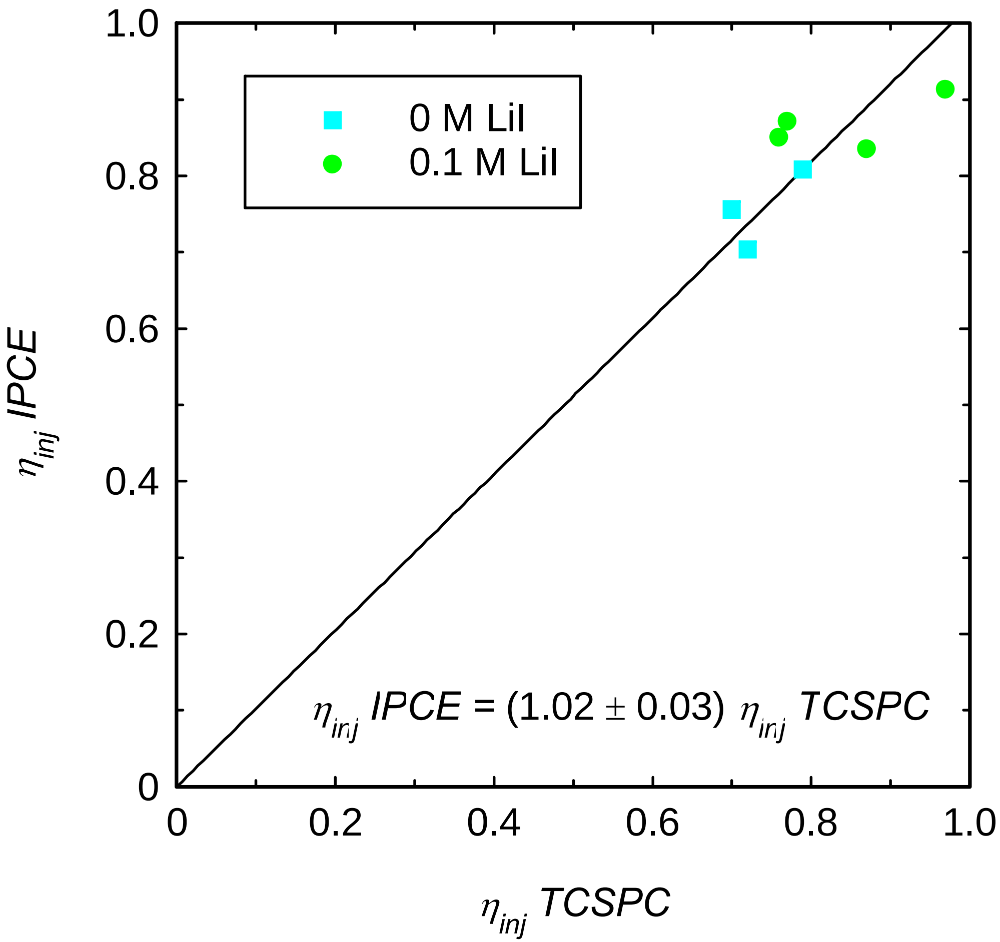
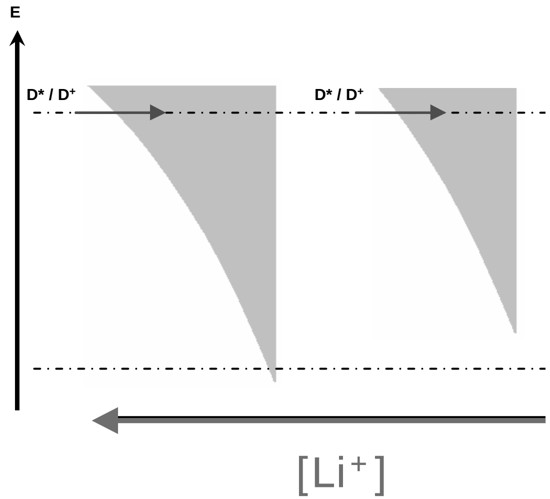
Time Correlated Single Photon Counting – η_{inj}

Identical cells fabricated using injecting and non injecting substrates (titania or zirconia) – emission quenched by injection





Li increases injection and collection

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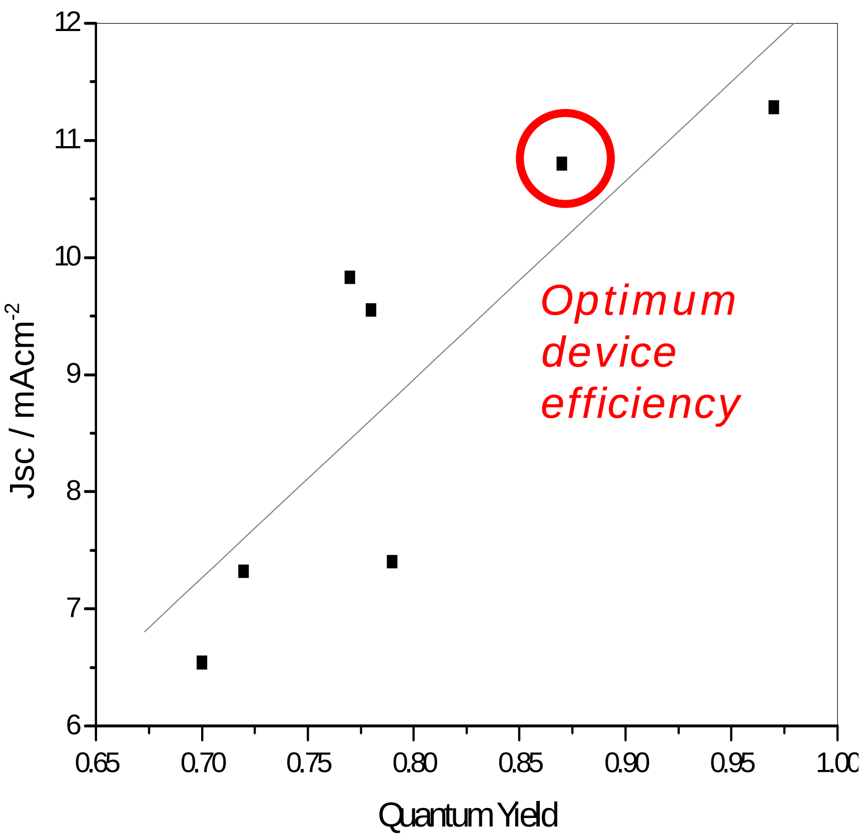
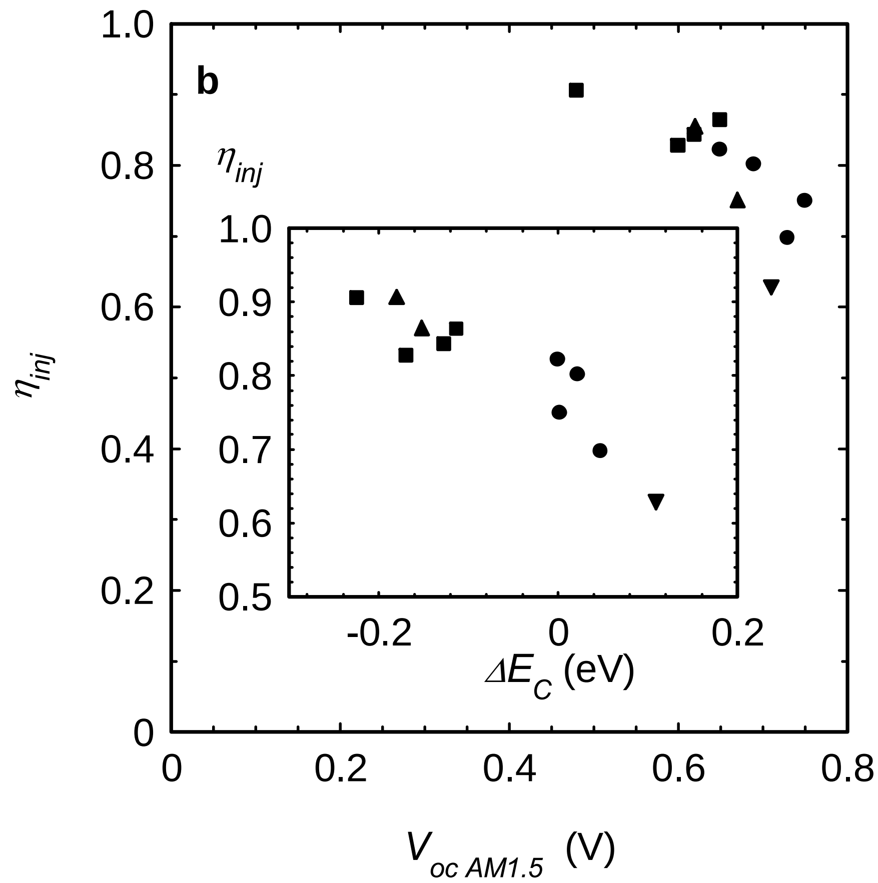
Highest η_{inj} does not optimise cell efficiency

TCSPC (*d* = 4 µm)

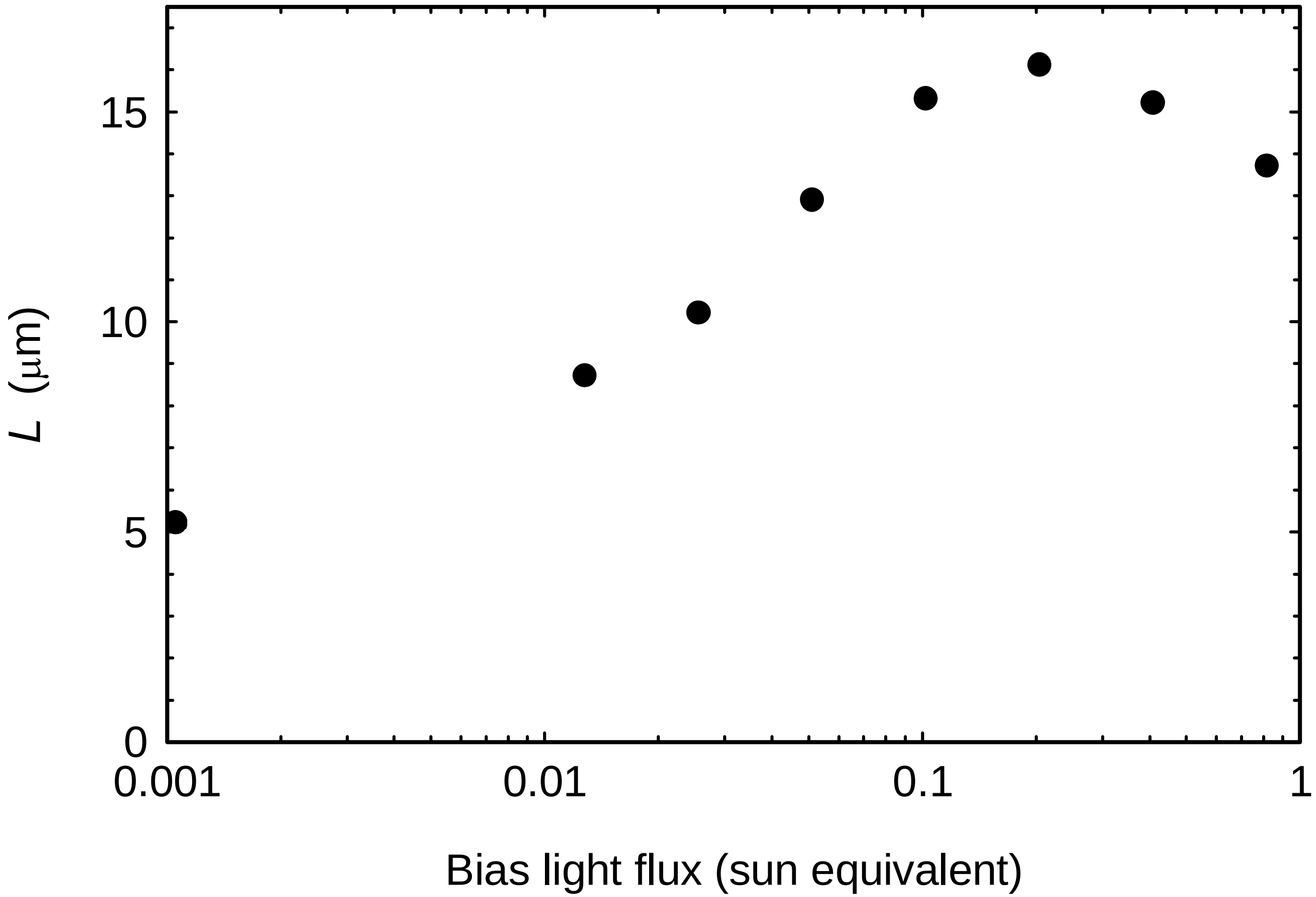


IPCE (*d* = 13 µm)

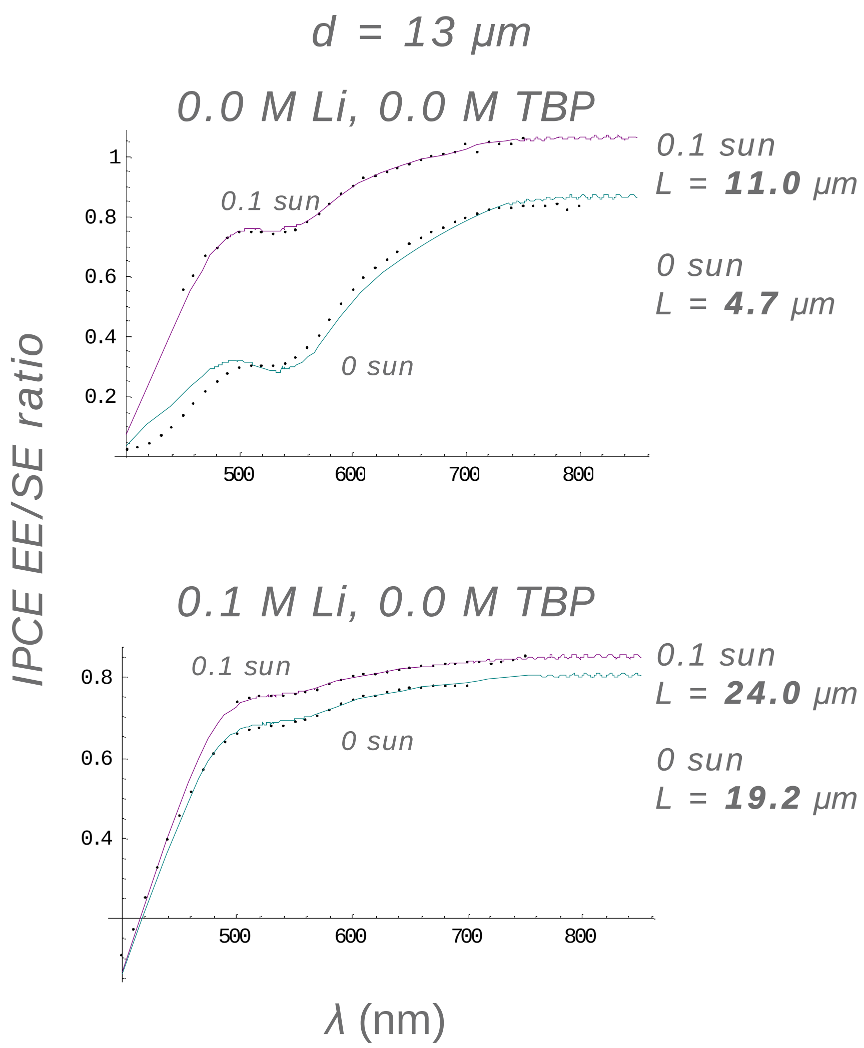


The effect of light intensity on *L*

d = 13 µm   0.0 M Li, 0.0 M TBP



The effect of light intensity on L



[illegible]

Bias light increases L

(mA cm-2)	Measured, 1 sun (Xe lamp)	No bias light	0.1 sun bias light
Cell	J_{sc}	$J_{AM1.5\ calc}$	$J_{AM1.5\ calc}$
0.0 M Li	7.5	4.5	**7.1**
0.1 M Li	11.4	11.4	**11.7**

Predicted photocurrents are closer to observed

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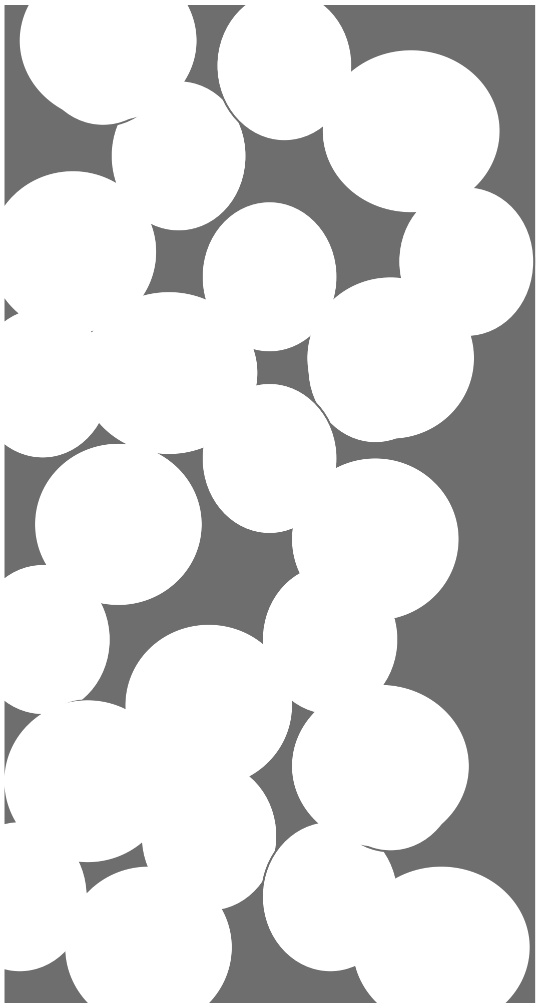
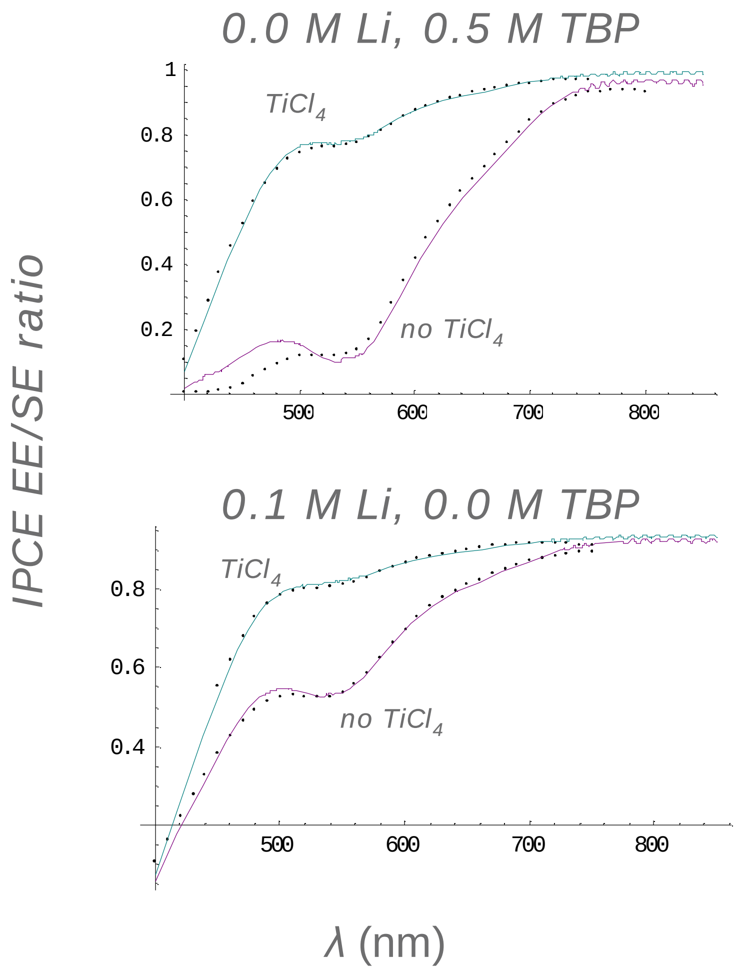
$TiCl_4$ treatment



d = 13 μm, no bias light



0.0 M Li, 0.5 M TBP

with $TiCl_4$
L = **14.6** μm, η_{inj} ~ 76 %
J_{sc} = 9.2 mA cm^{-2}

no $TiCl_4$
L = **1.9** μm, η_{inj} ~ 83 %
J_{sc} = 4.3 mA cm^{-2}

0.1 M Li, 0.0 M TBP

with $TiCl_4$
L = **21.7** μm, η_{inj} ~ 91 %
J_{sc} = 11.4 mA cm^{-2}

no $TiCl_4$
L = **7.9** μm, η_{inj} ~ 87 %
J_{sc} = 8.6 mA cm^{-2}

Is diffusion length a useful concept?

$$L = \sqrt{D_n \tau_n}$$

τ_n → 'effective' electron lifetime
D_n → 'effective' electron diffusion coefficient

Disordered system – multiple trapping model

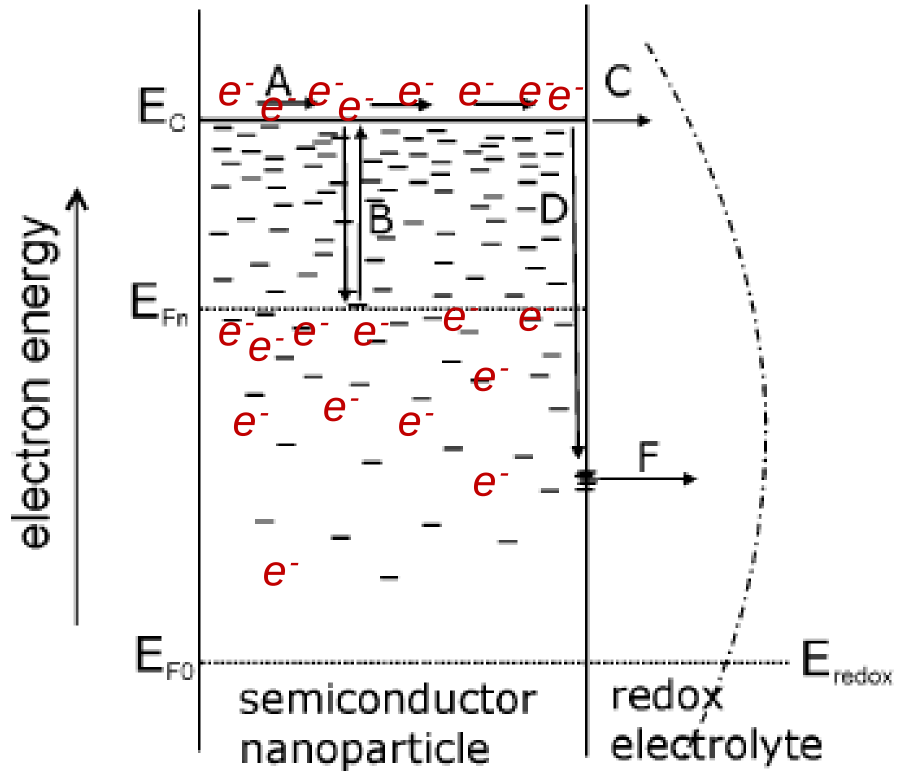
n_c → conduction band electron concentration

n_L → localised trapped electron concentration

Quasi-static approximation (e.g. Bisquert and Vikhrenko, 2004)

$$\frac{\partial n_L}{\partial t} = \frac{\partial n_L}{\partial n_c}\frac{\partial n_c}{\partial t}$$

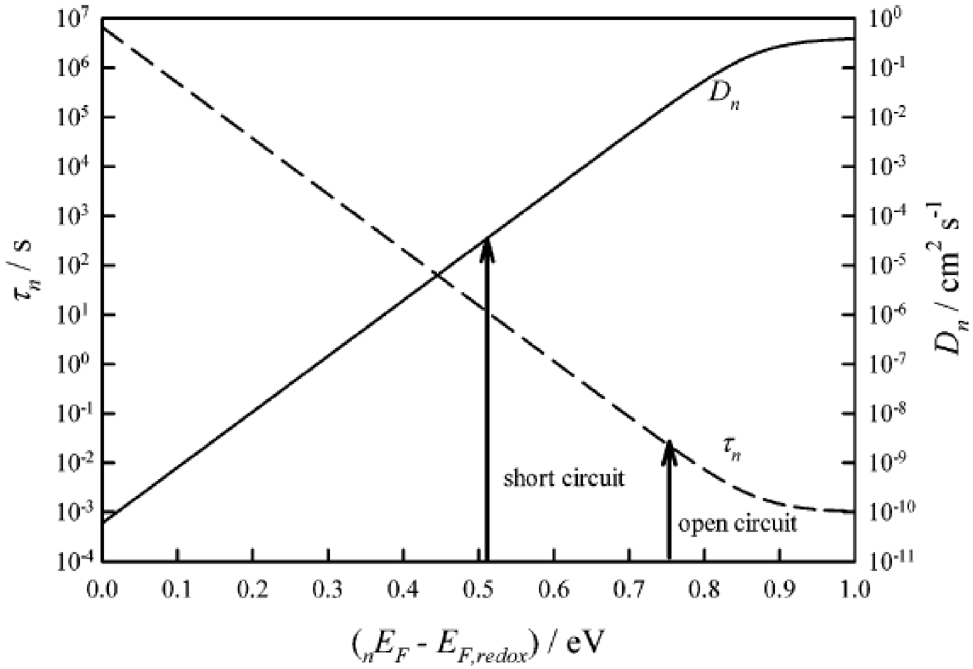
Rate of trapping and de-trapping fast relative to other processes in the cell



Diffusion Length from small perturbation methods

$\tau_n \rightarrow$ *effective electron lifetime*

$D_n \rightarrow$ *effective electron diffusion coefficient*



(Peter, 2006)

$$\sqrt{D_0 \tau_0} = \sqrt{D_n \tau_n}$$

L should be independent of n_c and thus x – if quasistatic model obeyed

$$L = \sqrt{D_n \tau_n}$$

Must use matched n measurements

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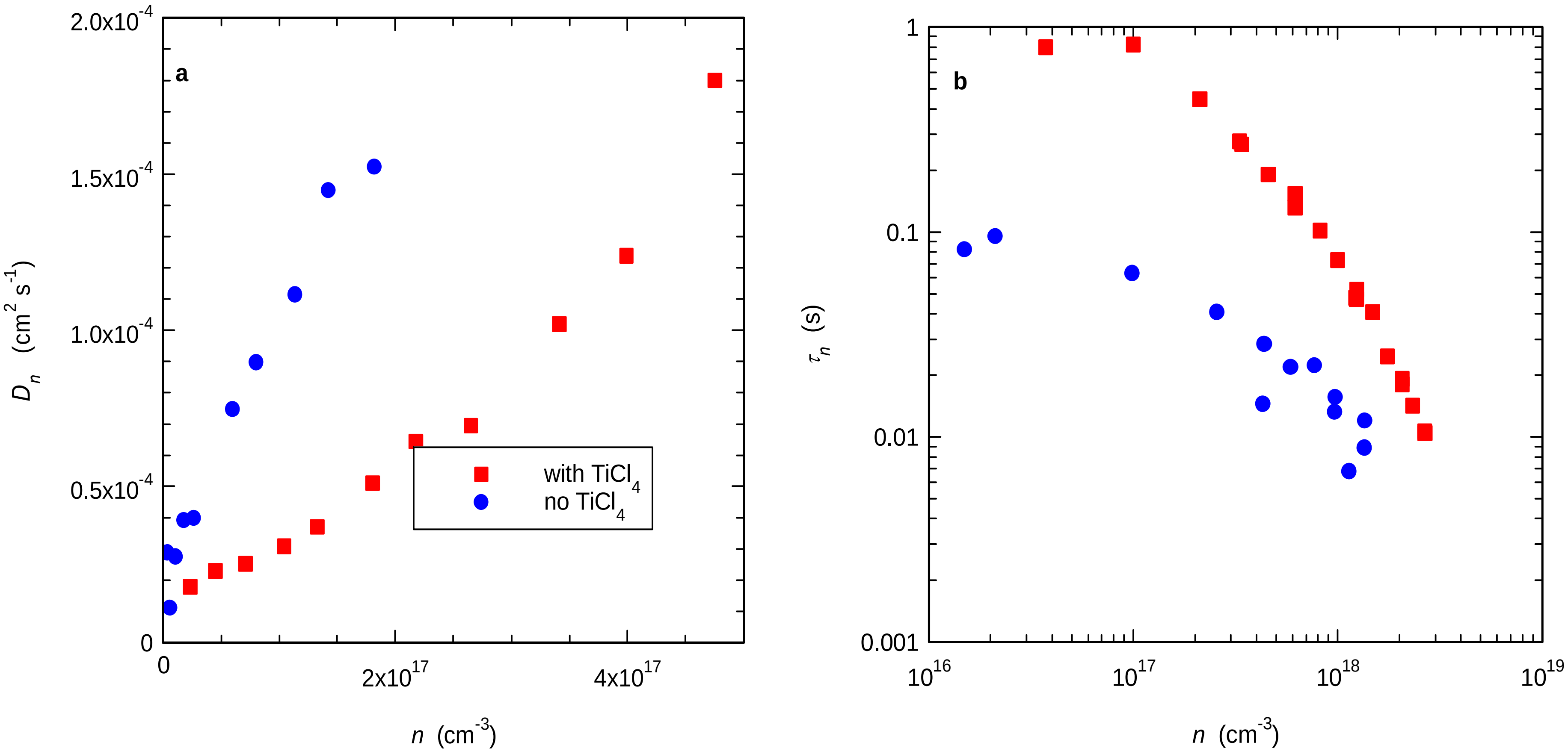
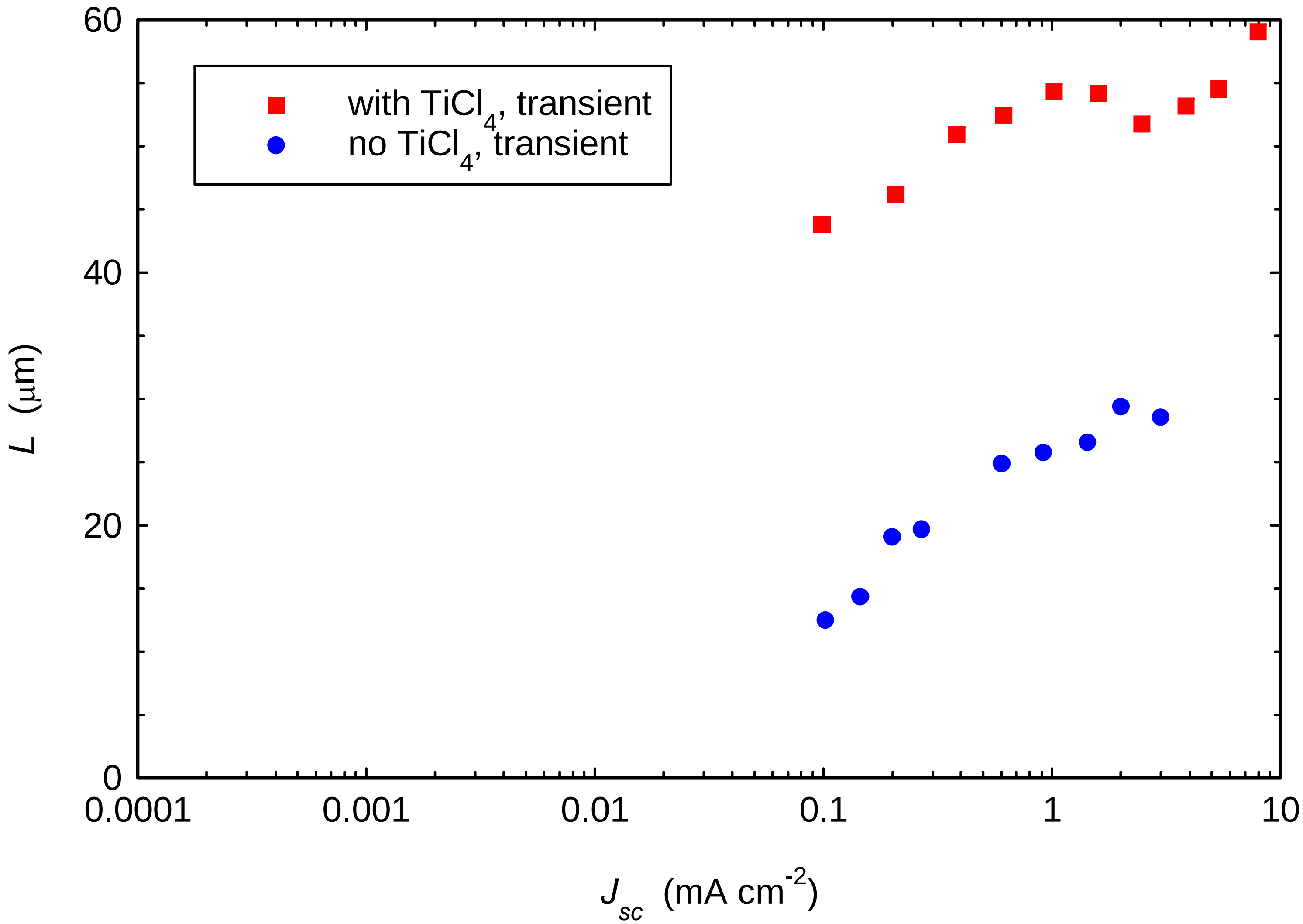
$TiCl_4$ treatment – short circuit transients

d = 13 µm   *0.0 M Li, 0.5 M TBP*

Drop in effective diffusion coefficient– but substantial increase in electron lifetime



$TiCl_4$ treatment – L



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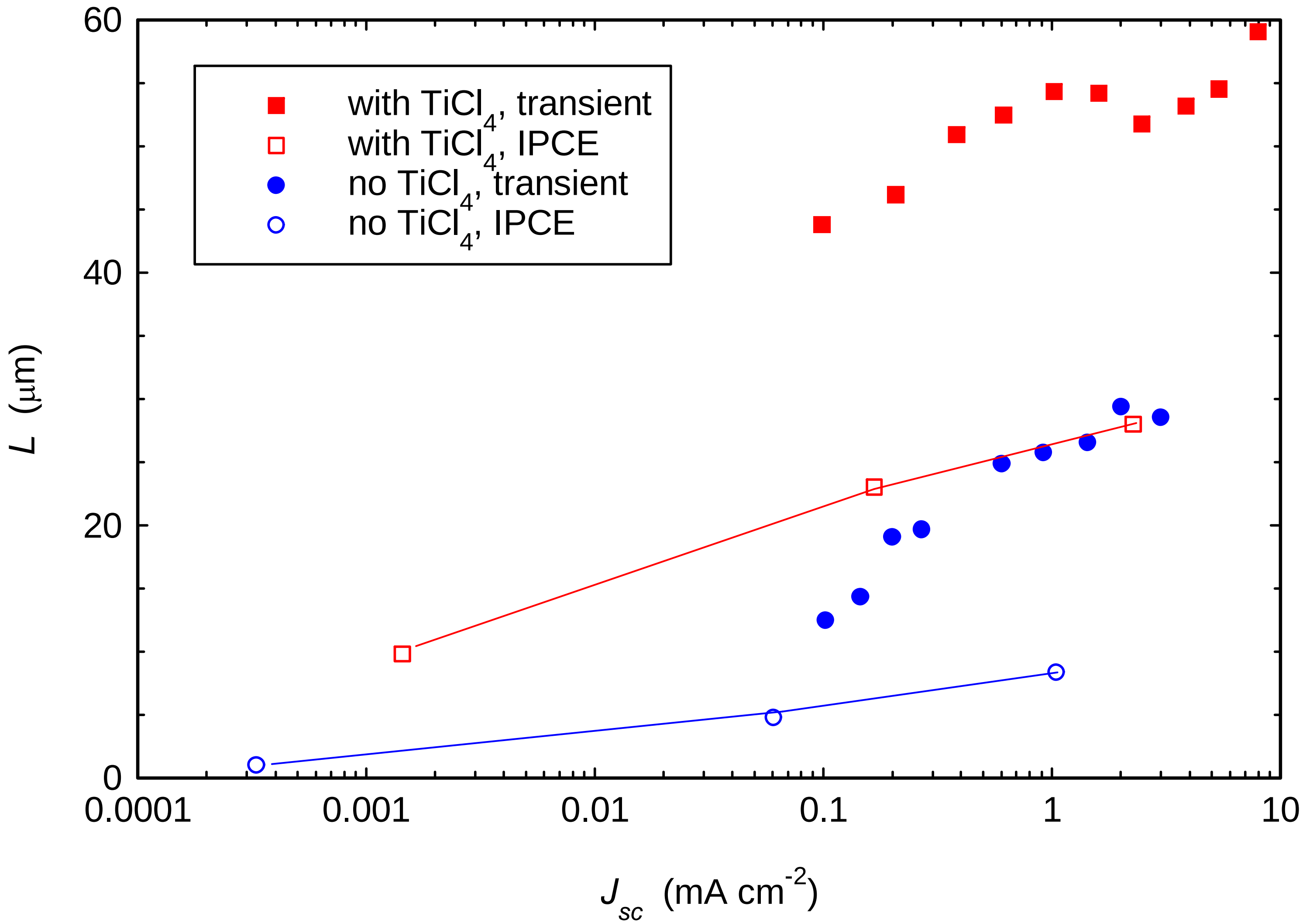
$TiCl_4$ treatment – L



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L_{IPCE} correctly predicts photocurrent

$$j_{sc} = q\Phi\, \overline{\eta_{LH}}\, \eta_{inj}\, \overline{\eta_{col}}$$

$q\Phi$ = 68.3 mA cm^{-2} (λ < 4000 nm)

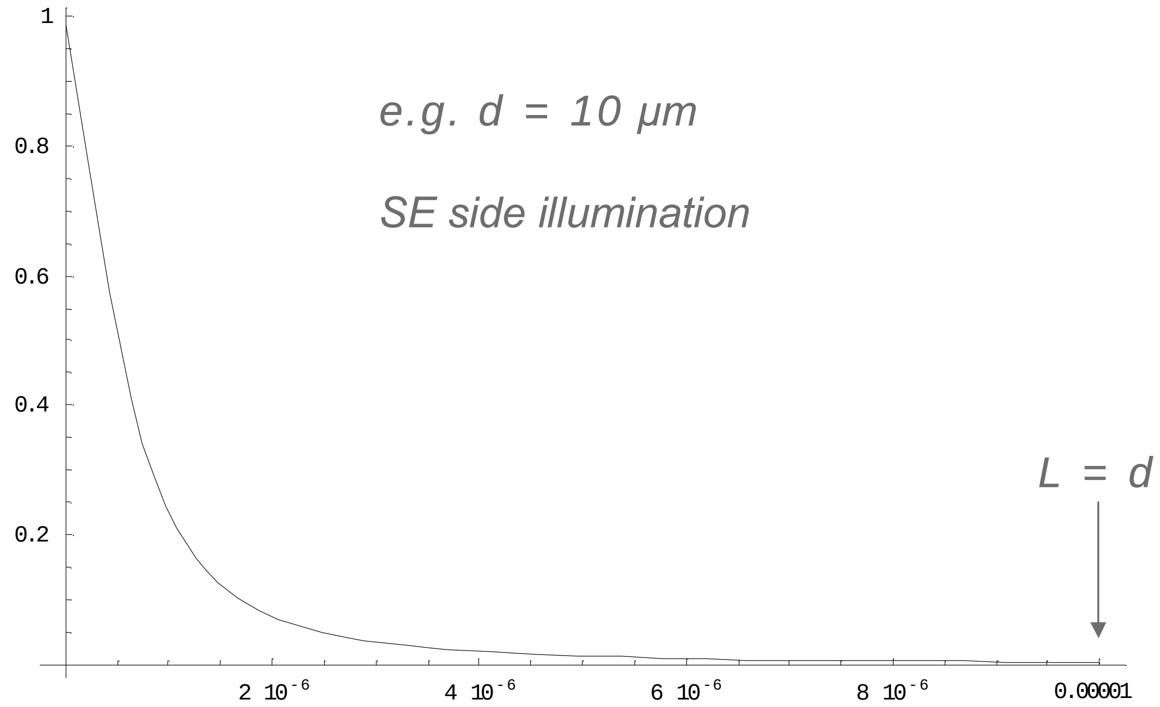
Measured ($j_{sc\ AM1.5}$) and calculated ($j_{sc\ calc}$) photocurrents for two cells (d = 13.5 µm) prepared with and without the $TiCl_4$ treatment under 'front' and 'back' illumination (SE and EE side).

cell, illumination direction	$j_{sc\ AM1.5}$ **[measured] (mA cm^{-2})**	L_{IPCE} (µm)	L_{trans} (µm)	$\overline{\eta_{LH}}$ [AM1.5]	η_{inj}	$\overline{\eta_{col}}$ [L_{IPCE}]	$\overline{\eta_{col}}$ [L_{trans}]	$j_{sc\ calc}$ **[L_{IPCE}] (mA cm^{-2})**	$j_{sc\ calc}$ [L_{trans}] (mA cm^{-2})
no $TiCl_4$, SE	**5.2**	8.3	20	0.18	0.63	0.67	0.91	**5.0**	7.1
no $TiCl_4$, EE	**3.8**	8.3	20	0.16	0.63	0.49	0.85	**3.4**	5.9
with $TiCl_4$, SE	**8.9**	28	55	0.20	0.69	0.95	0.99	**8.9**	9.3
with $TiCl_4$, EE	**7.8**	28	55	0.18	0.69	0.91	0.98	**7.7**	8.3

What influence does *L* have on a typical cell?

$\overline{\eta_{col}}$ = *Fraction of injected charge recombining before collection under AM1.5 illumination and N719 absorption*

$1 - \overline{\eta_{col}}$



L (m)

Recombination losses only significant when *L* < *d*, so not much for 'front' illumination

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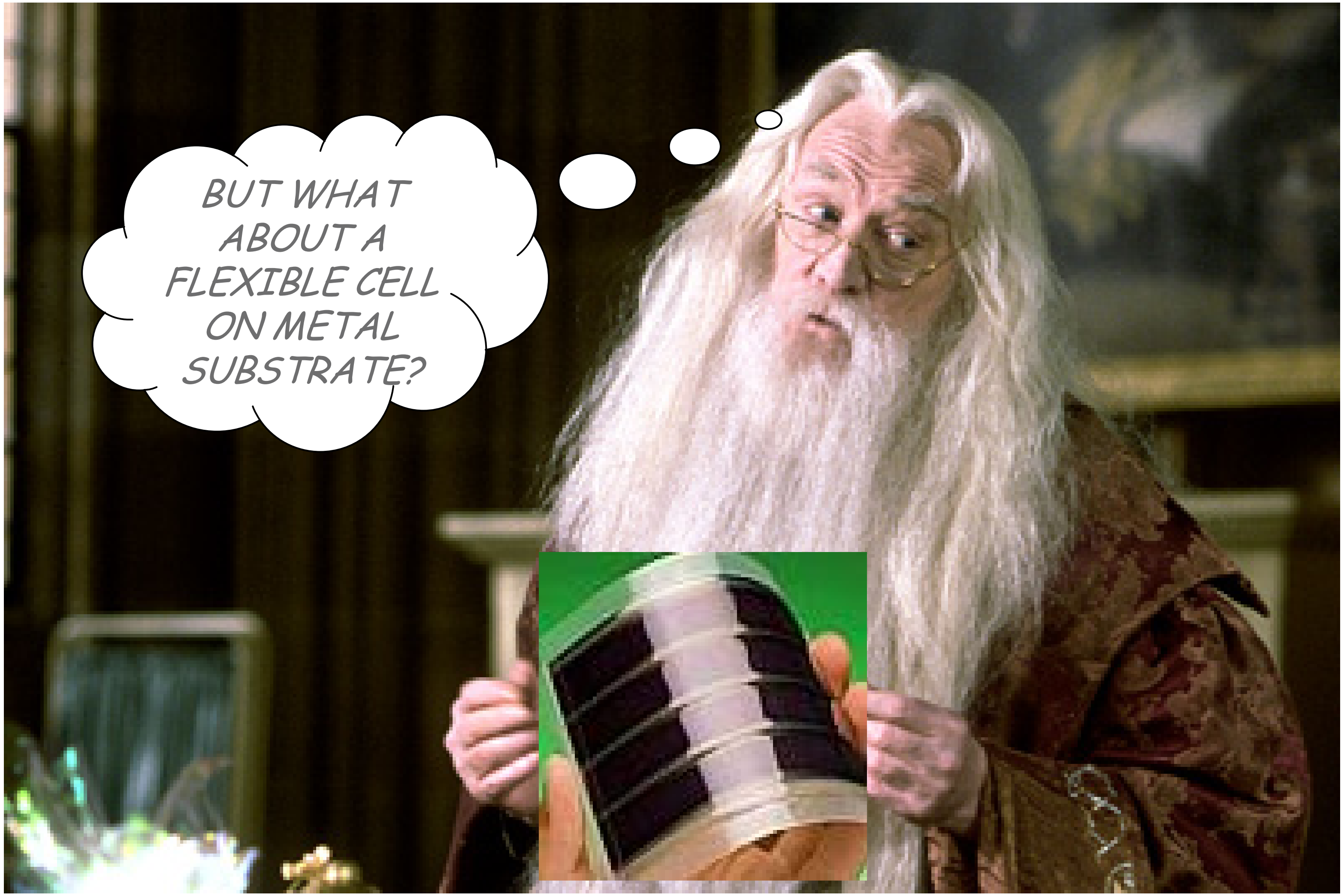
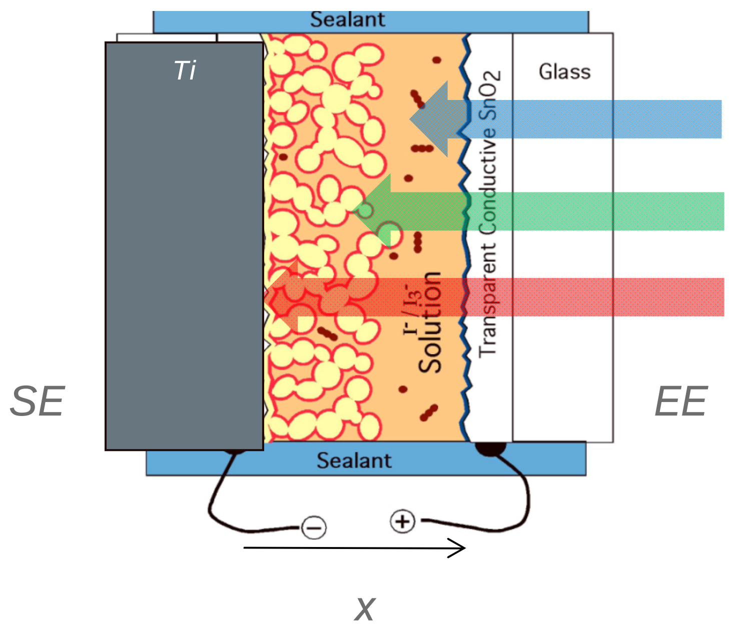
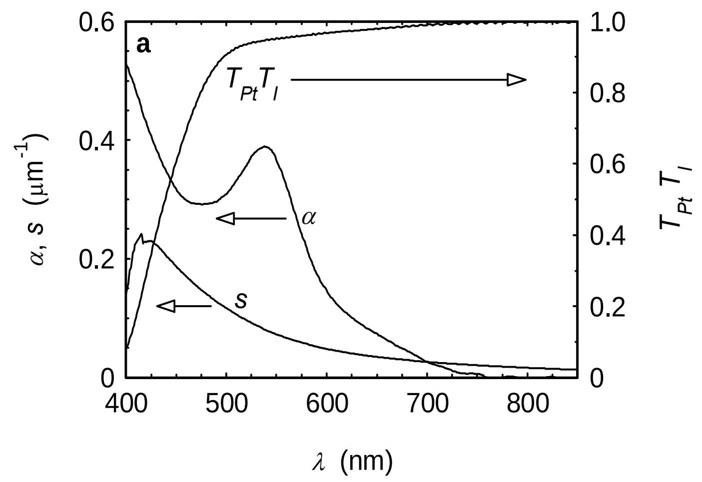
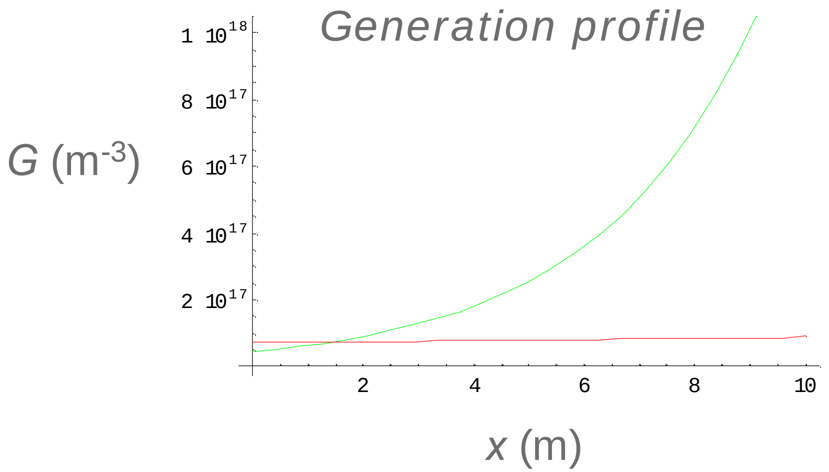
What influence does *L* have on a typical cell?



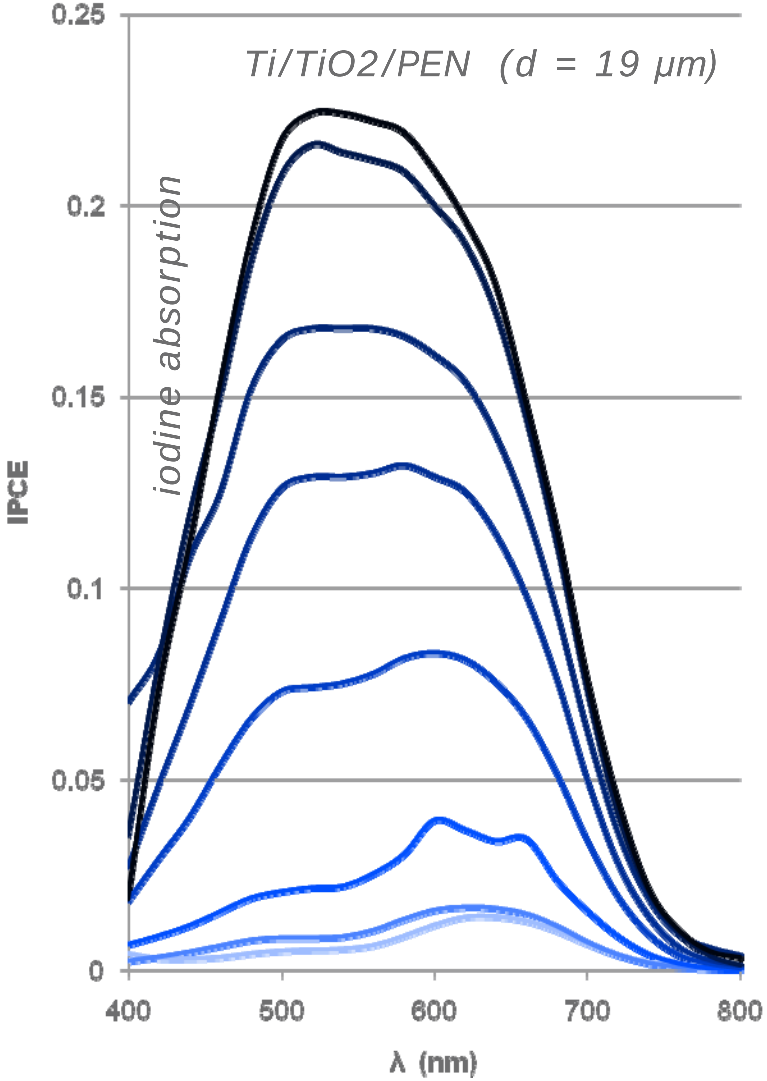
Metal substrates – EE side only illumination







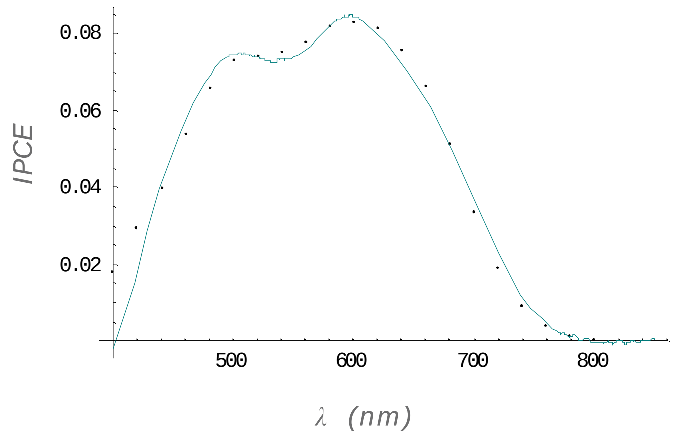
EE side only illumination – metal substrates



Bias light increases J_{sc} ($mA\ cm^{-2}$)

- 7.7E-05
- 3.4E-04
- 3.2E-03
- 3.0E-02
- 1.1E-01
- 2.4E-01
- 1.0E+00
- 2.1E+00

2 parameter fit:
L and loss (η_{inj} and optical)



J_{sc} = 0.03 $mA\ cm^{-2}$
L = 7.6 μm
loss = 0.35

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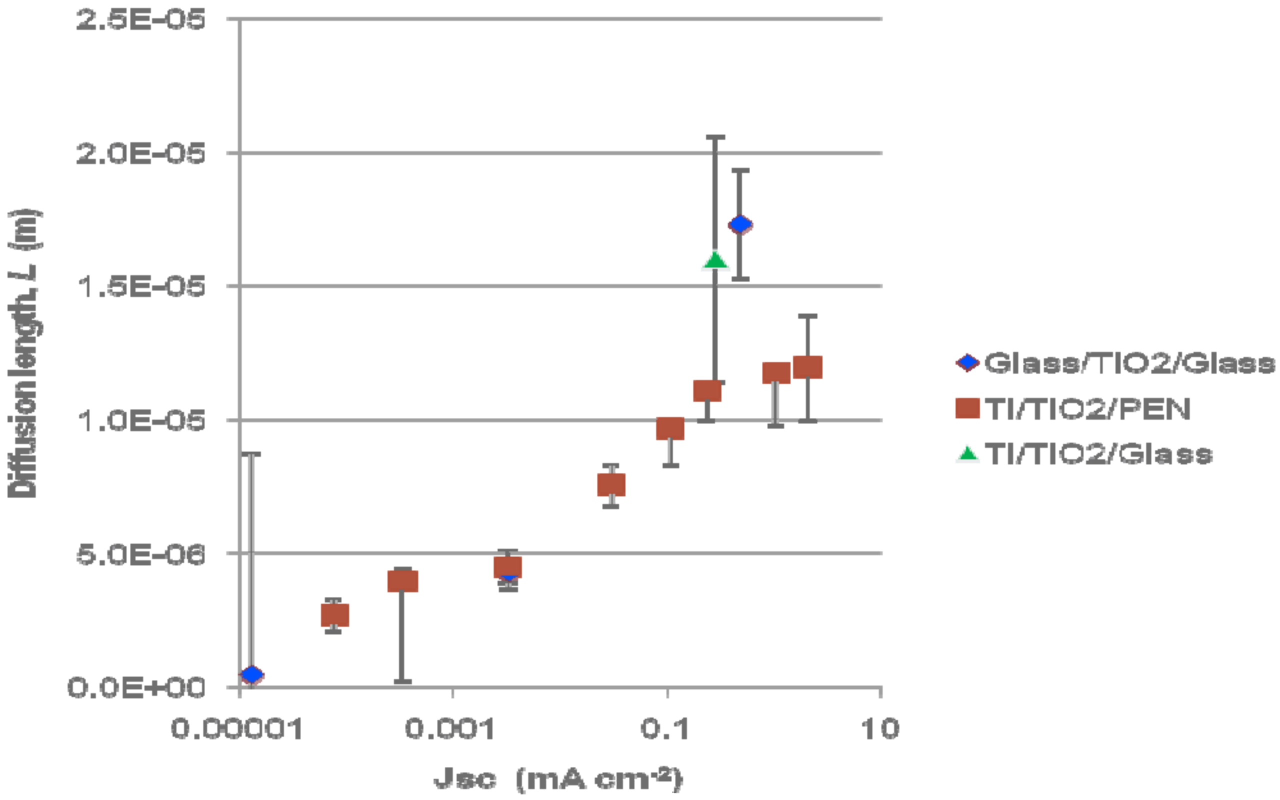
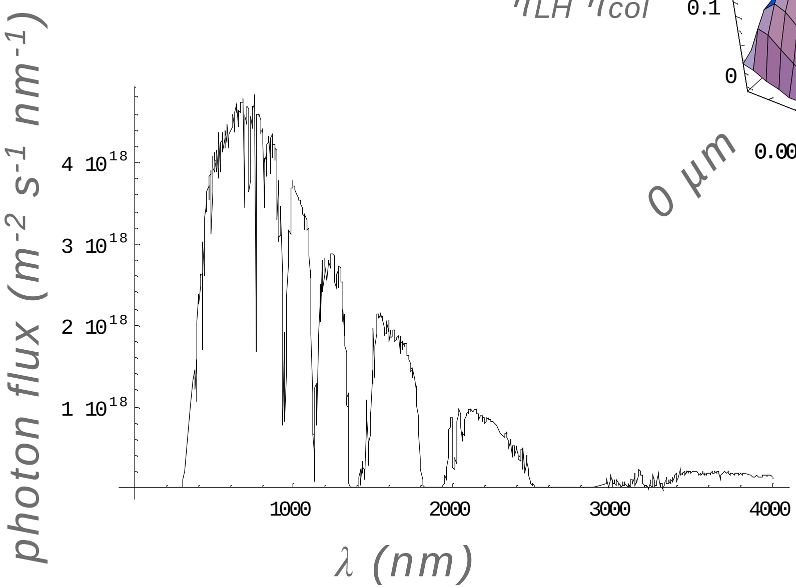
EE side only illumination – metal substrates

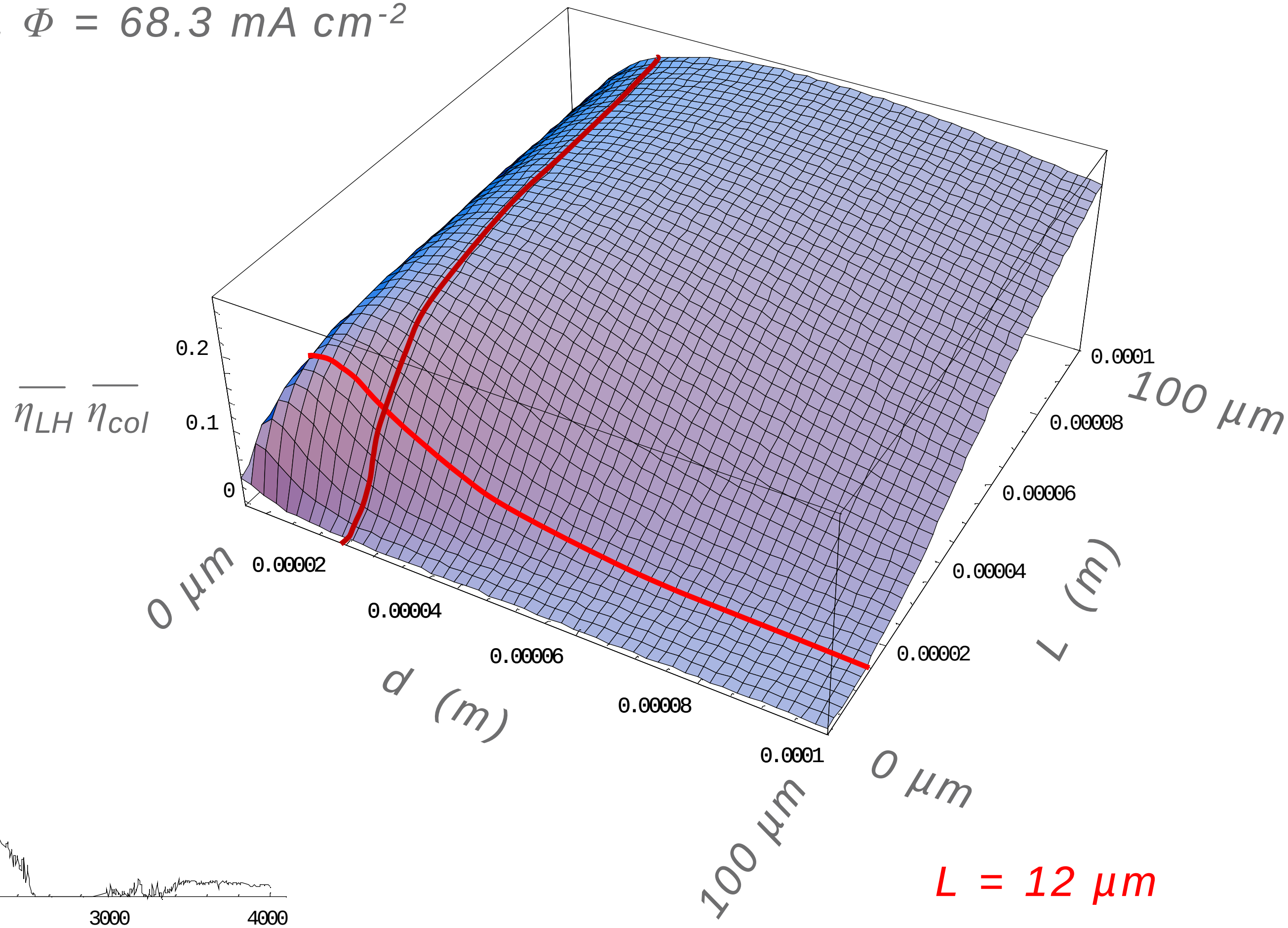


Collection efficiency dependence on *d* and *L*

AM1.5 solar current, Φ = 68.3 mA cm^{-2}

Assume α_{N719}





L = 12 µm

Ti/TiO2/PEN (d = 19 µm)

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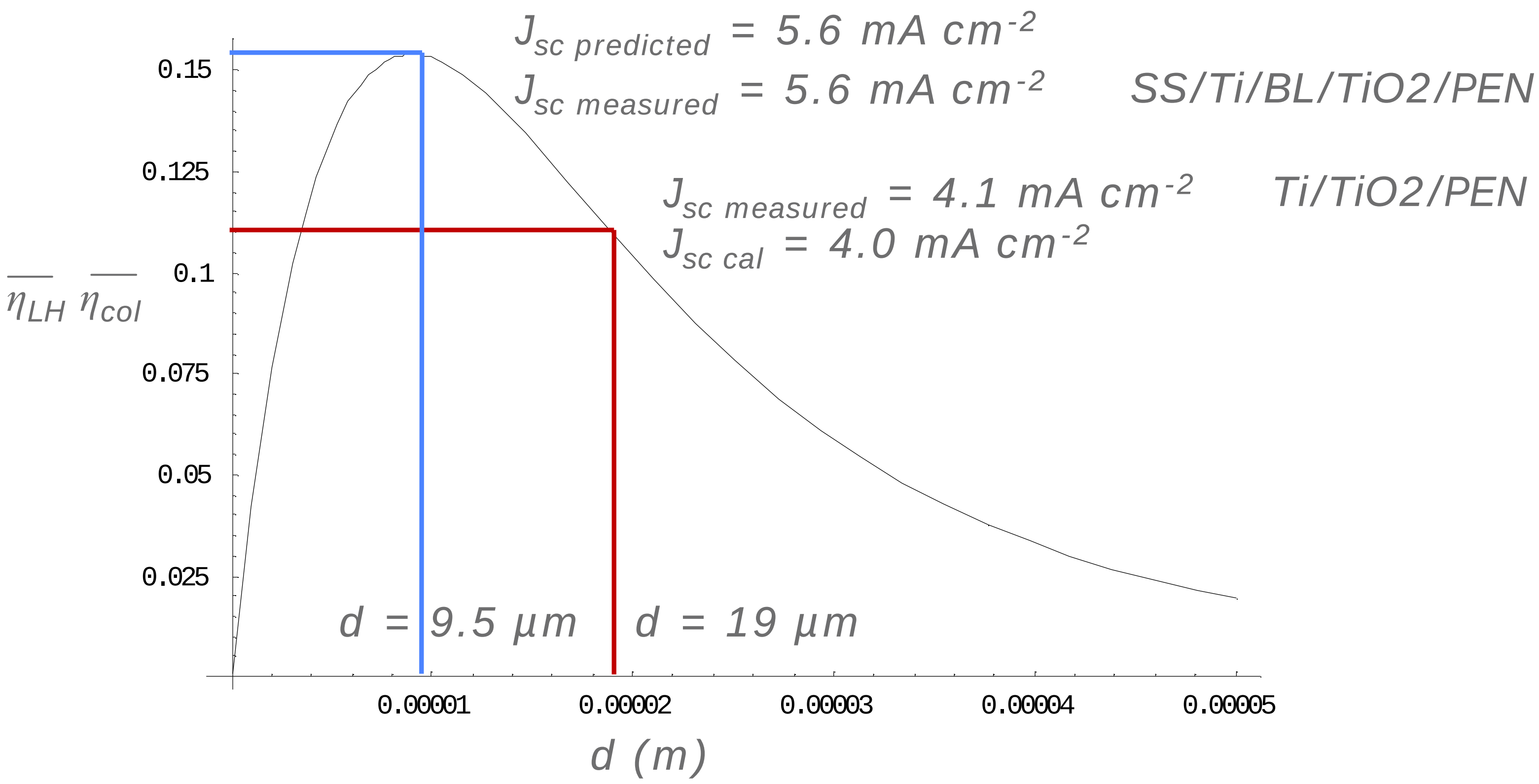
Optimising cell thickness given *L*

$L = 12\ \mu m$



$$J_{sc\ calc} = \Phi\ \overline{\eta_{inj}}\ \eta_{inj}\ \overline{\eta_{col}}$$

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Comparison of dyes: TG6 with K19

A New Ruthenium-Polypyridyl Dye "TG6" Whose Performance In Dye Sensitized Solar Cells Is Surprising Close To That Of The "N719", The Dye The No-One Has Managed To Beat In 17 Years

Stronger absorption, higher photocurrent than N719

Farah Matar, Tarek H. Ghaddar et al., accepted JMC

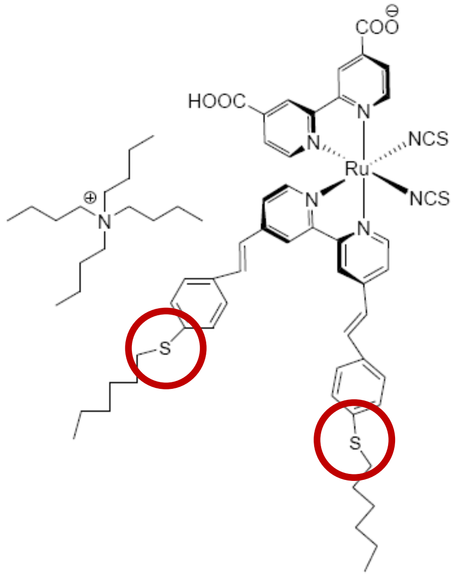


Figure 3.3 Structure of TG6

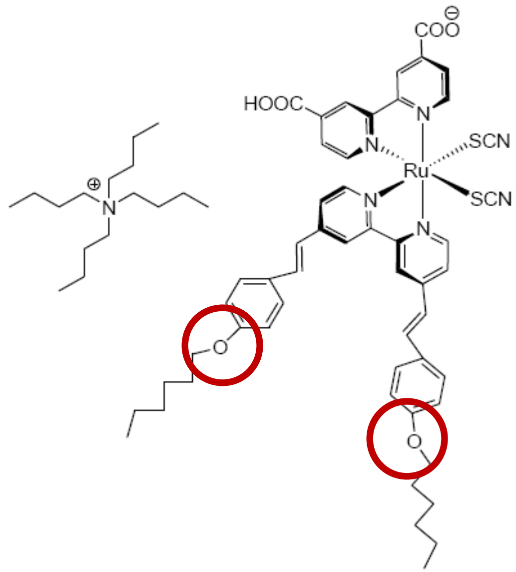
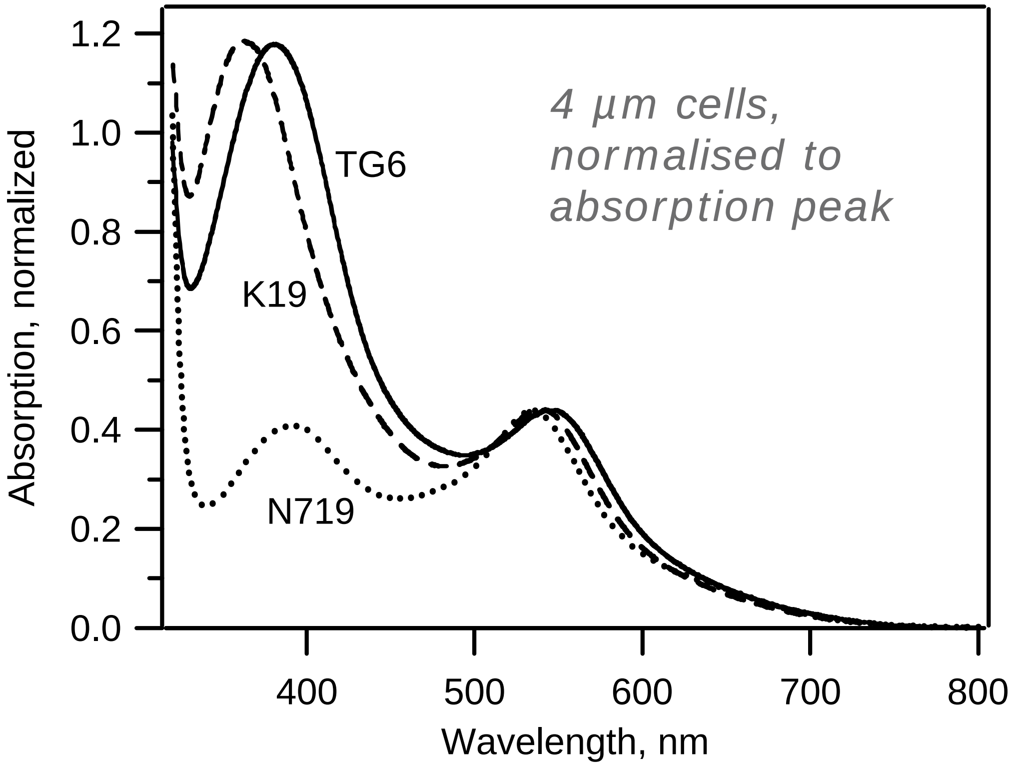
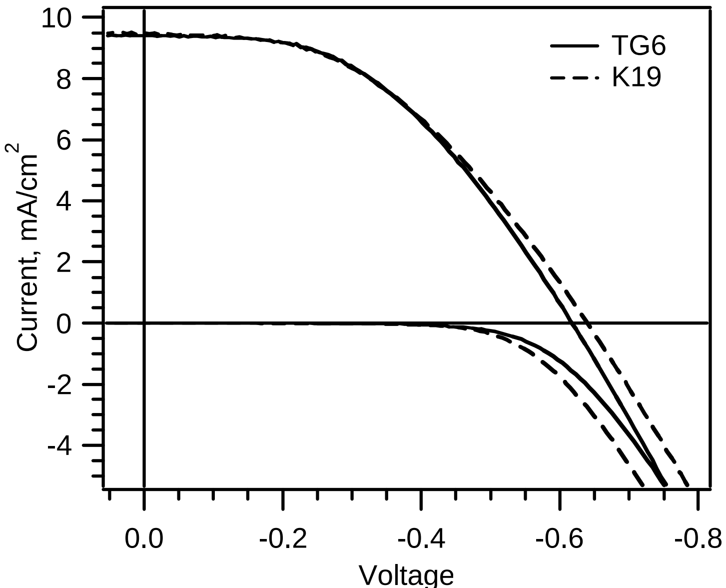


Figure 3.4 x Structure of K19

- TG6 – S
- K19 – O

Similar absorbance – lower photovoltage

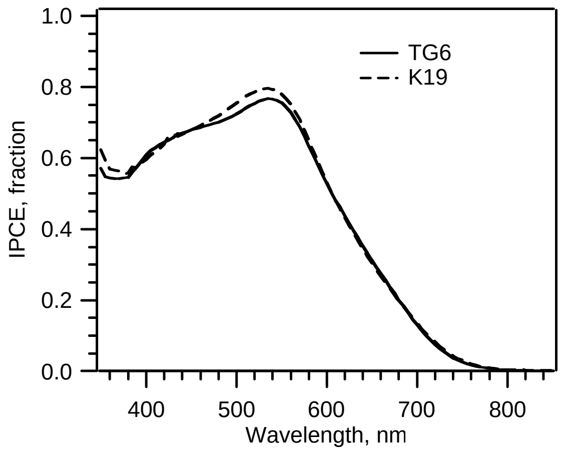




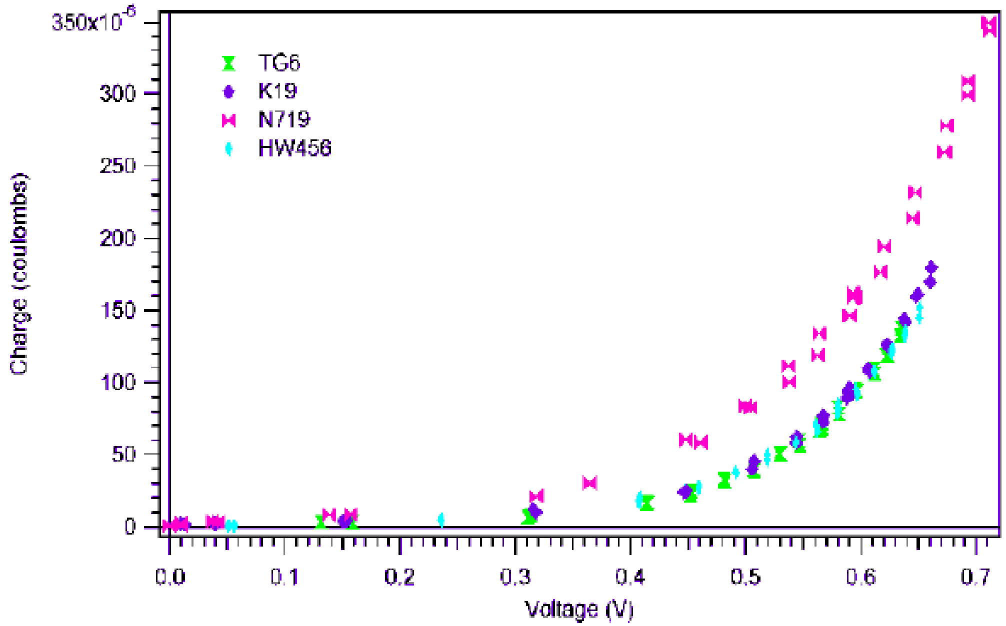
α	TG6 ~ K19 > N719
J_{sc}	K19 ~ TG6 > N719
V_{oc}	N719 > K19 > TG6

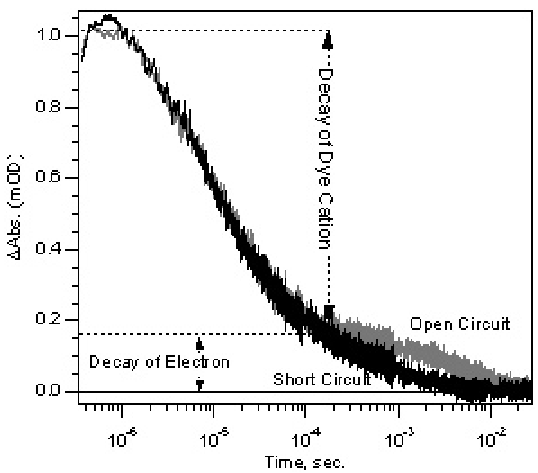
Dye	J_{sc}/mAcm-2	V_{oc}/V
N719	8.14	0.71
TG6	10.05	0.64
K19	10.43	0.66

What is the influence of O → S for K19 and TG6?



Injection similar

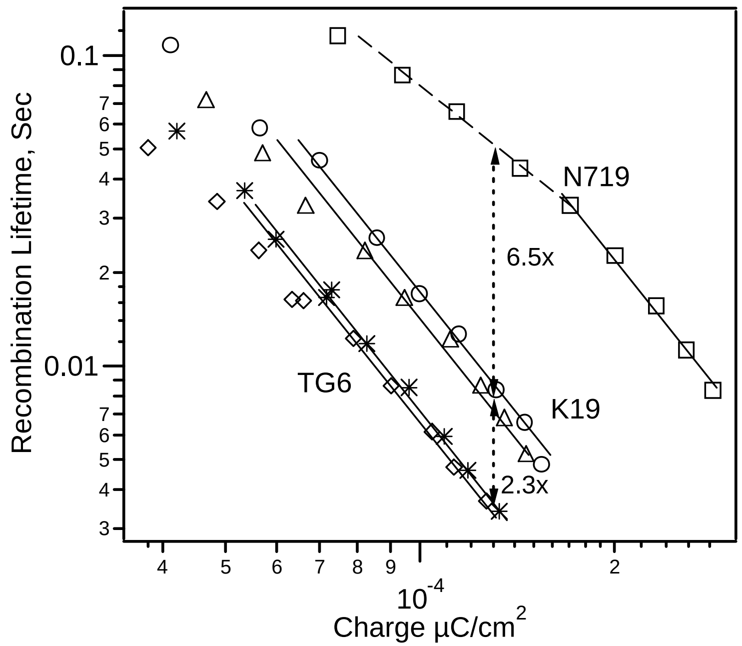


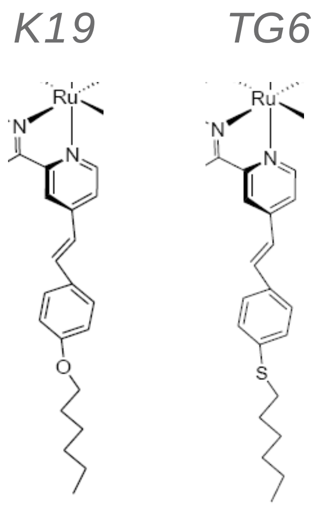


Dye regeneration similar

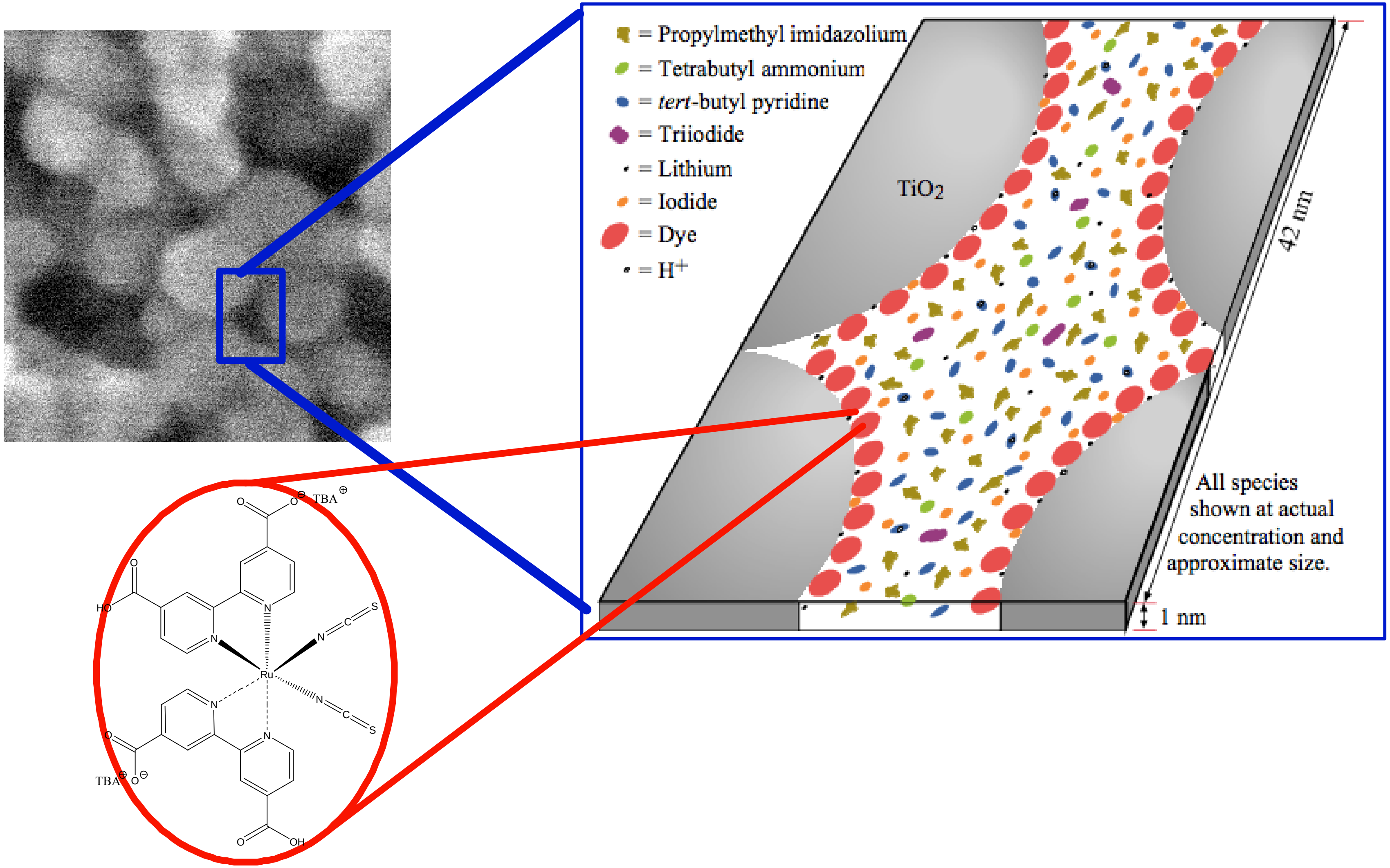
Same band edge positions
→same field between TiO_2 and electrolyte
→same driving force for recombination

What is the influence of O → S for K19 and TG6?





What is the influence of O → S for K19 and TG6?



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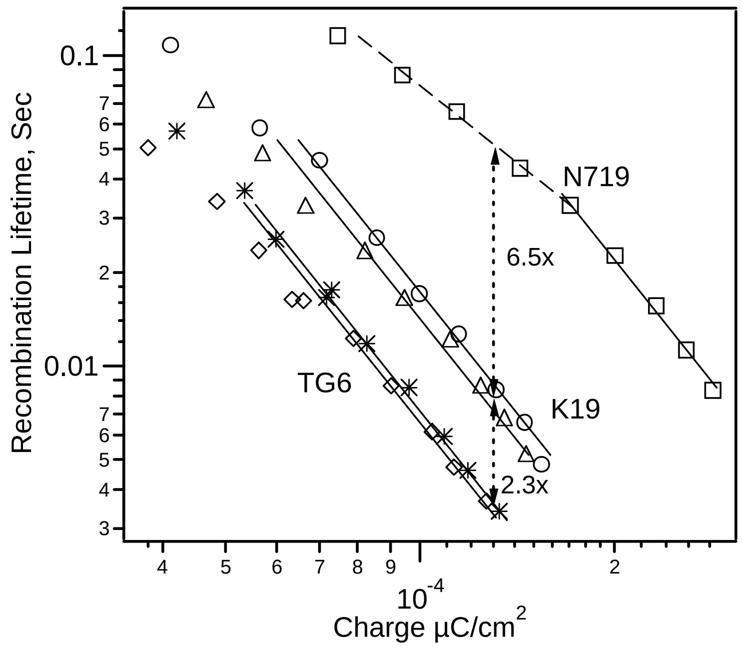
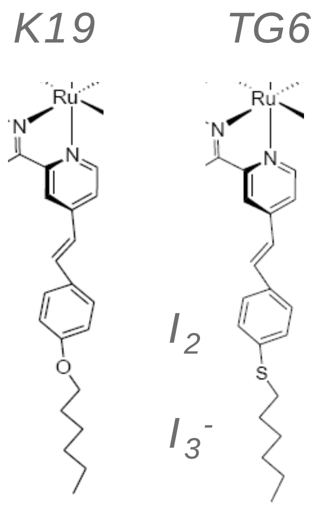
What is the influence of O → S for K19 and TG6?



Recombination twice as fast in TG6 relative to K19

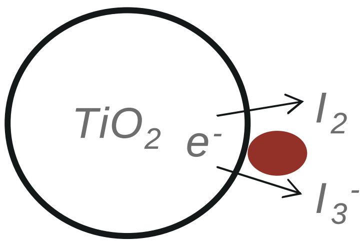


Iodine binding may be responsible

The iodine binding constants in heptane:

Ethyl ether ~ 6
Ethyl thioehter ~ 200
factor of 30 difference

Similar in delocalised systems with lower constants



Rate increase by increased concentration or reduced activation barrier

The binding is thought to occur at the 'heteroatom' lone pair even if delocalised
→ S has a lower electron affinity than O
→ TG6 more likely to bind iodine than K19 close to cell interface

Conclusions

- Diffusion length and electron injection efficiency can be derived from IPCE measurements and SPC, light dependence observed

- Both injection and collection are important optimisation parameters (e.g. via electrolyte additives)

- IPCE typically shows intensity dependence

- Treatment of the TiO_2 film with $TiCl_4$ increases L – particularly for poorly performing cells

- Features of dye molecules appear to influence recombination rates through iodine binding

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IPCE fitting expressions

$$\frac{\eta_{EE}}{\eta_{SE}} = \frac{T_{Pt}\,T_I\left[(L(\alpha+\alpha_I)+1)\mathrm{e}^{\frac{2d}{L}} - 2L(\alpha+\alpha_I)\mathrm{e}^{d\left(\alpha+\alpha_I+\frac{1}{L}\right)} + L(\alpha+\alpha_I)-1\right]}{(L(\alpha+\alpha_I)-1)\mathrm{e}^{d\left(\alpha+\alpha_I+\frac{2}{L}\right)} + (L(\alpha+\alpha_I)+1)\mathrm{e}^{d(\alpha+\alpha_I)} - 2L(\alpha+\alpha_I)\mathrm{e}^{\frac{d}{L}}}$$

$$\eta_{SE} = \frac{(1-R)L\,\eta_{inj}\,\alpha\mathrm{e}^{-d(\alpha+\alpha_I)}\left[(L(\alpha+\alpha_I)-1)\mathrm{e}^{d\left(\alpha+\alpha_I+\frac{2}{L}\right)} + (L(\alpha+\alpha_I)+1)\mathrm{e}^{d(\alpha+\alpha_I)} - 2L(\alpha+\alpha_I)\mathrm{e}^{\frac{d}{L}}\right]}{\left(\mathrm{e}^{\frac{2d}{L}}+1\right)\left[L^2(\alpha+\alpha_I)^2-1\right]}$$

$$\eta_{EE} = \frac{(1-R)\,T_{Pt}\,T_I L\,\eta_{inj}\,\alpha\mathrm{e}^{-d(\alpha+\alpha_I)}\left[(L(\alpha+\alpha_I)+1)\mathrm{e}^{\frac{2d}{L}} - 2L(\alpha+\alpha_I)\mathrm{e}^{d\left(\alpha+\alpha_I+\frac{1}{L}\right)} + L(\alpha+\alpha_I)-1\right]}{\left(\mathrm{e}^{\frac{2d}{L}}+1\right)\left[L^2(\alpha+\alpha_I)^2-1\right]}$$