Resolving electron injection from singlet fission-borne triplets into mesoporous transparent conducting oxides

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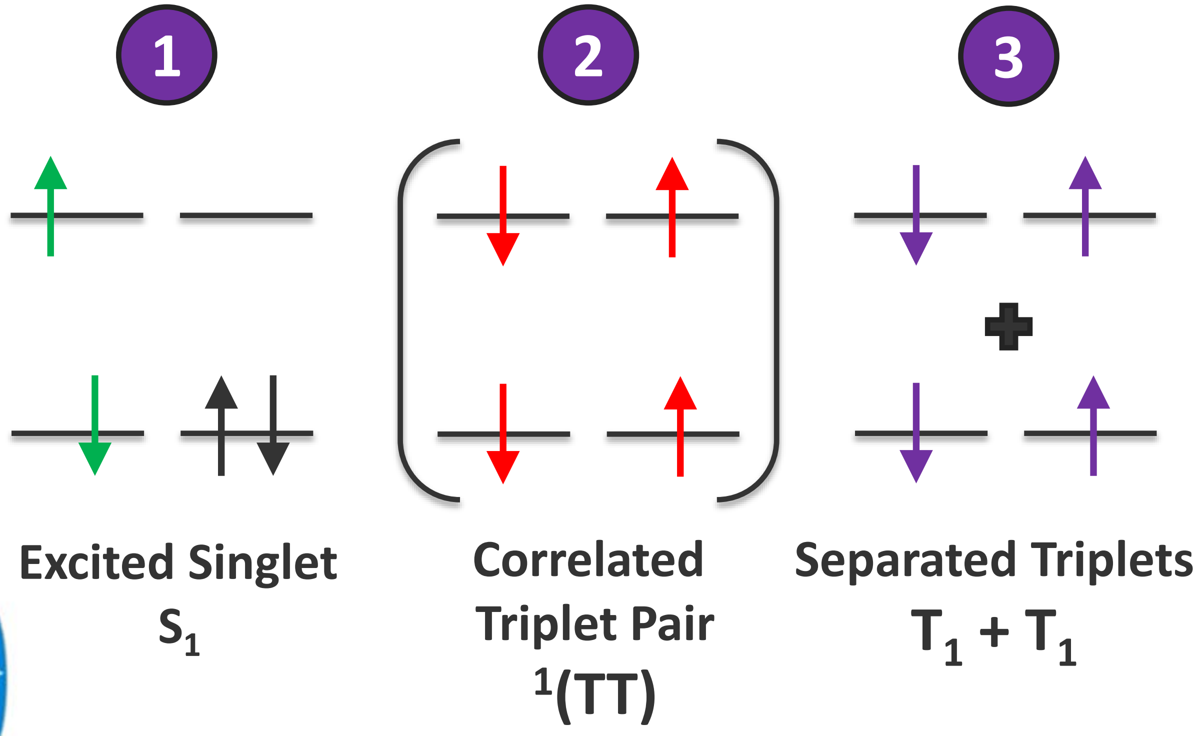
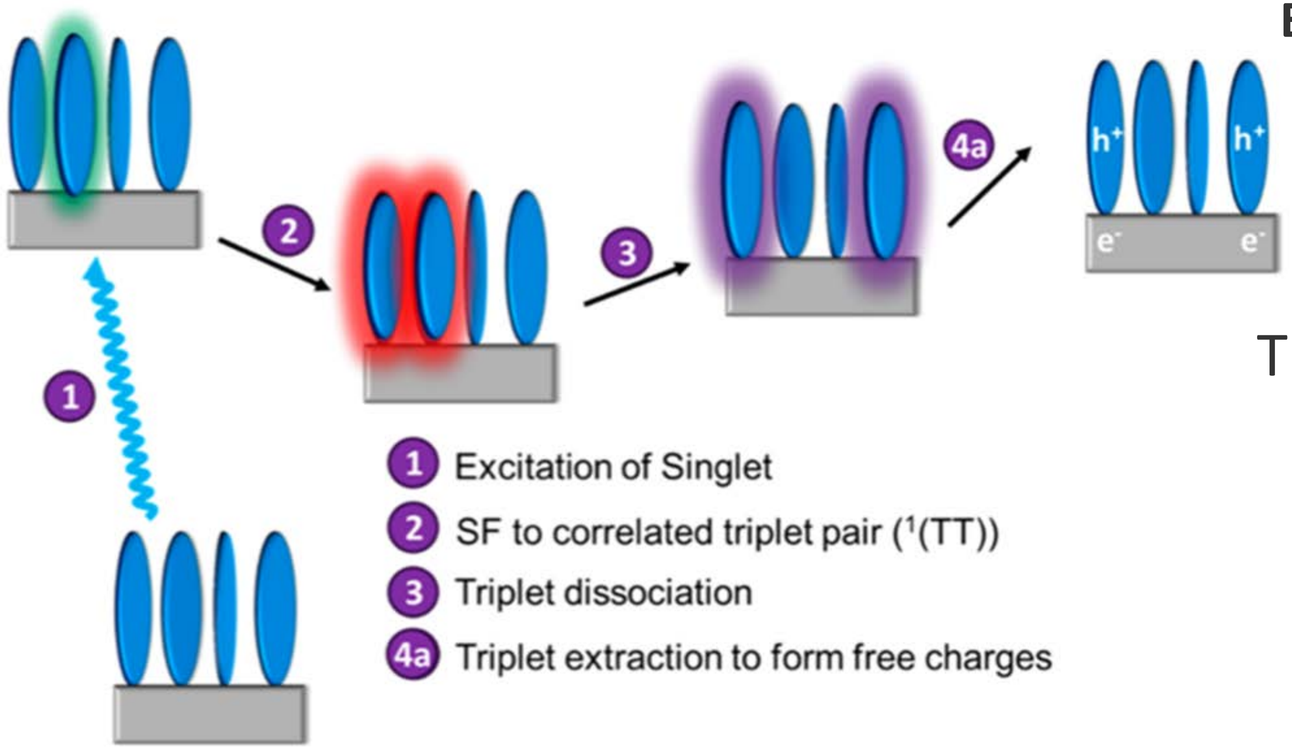
Singlet Fission-Extracting Triplets

Singlet Fission (SF) is the process of transforming one photoexcited singlet state into two lower energy triplet (T_1) excited states on neighboring molecules.





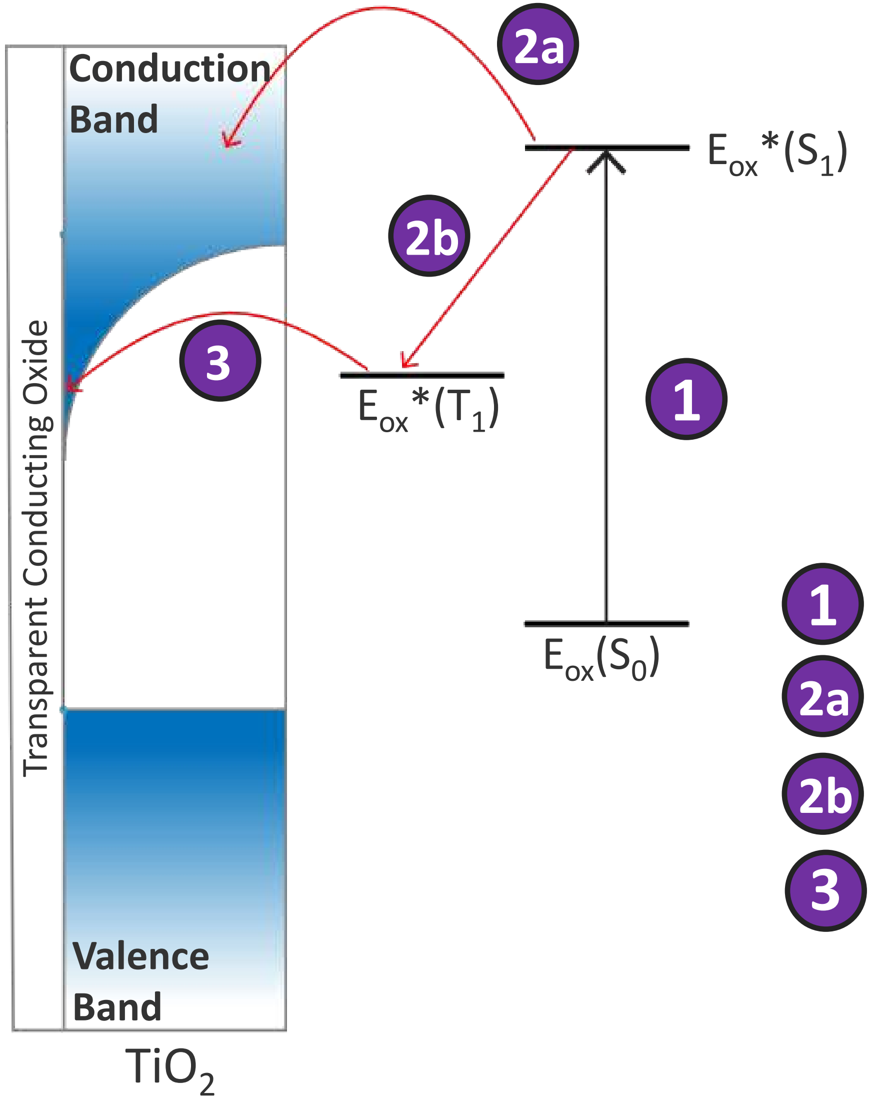
The energy requirements for **SF** are such that:

$$E(S_1) \approx 2E(T_1)$$

Low energy triplets often leads to issues with generating sufficient driving force for charge transfer.

Gish, M.K., Pace, N.A.; Rumbles, G., Johnson, J. C., *et.al., J. Phys. Chem. C*, **2019**, *123,* 3923-3934.

SF-Dye-Sensitized Solar Cells



Historically, **competition** from singlet electron injection and low driving forces **inhibit** efficient triplet electron injection.

1. Photoexcitation
2a. Electron Injection from the Singlet Excited State (“Singlet Injection”)
2b. Singlet Fission
3. Electron Injection from the Triplet Excited State (“Triplet Injection”)

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*Transient absorption done under dry conditions

Singlet Fission DSSCs (SF-DSSCs)

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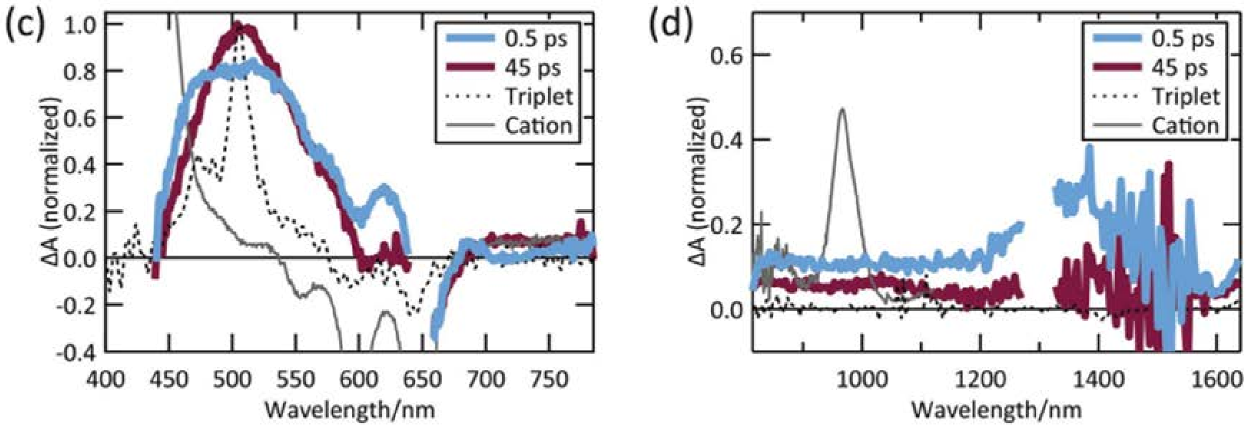
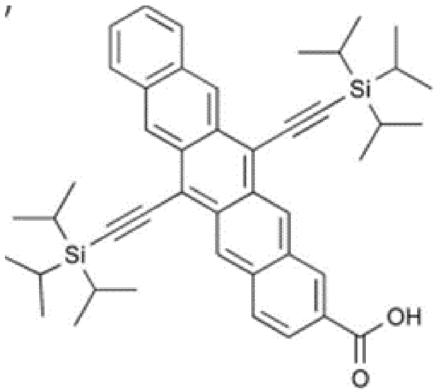
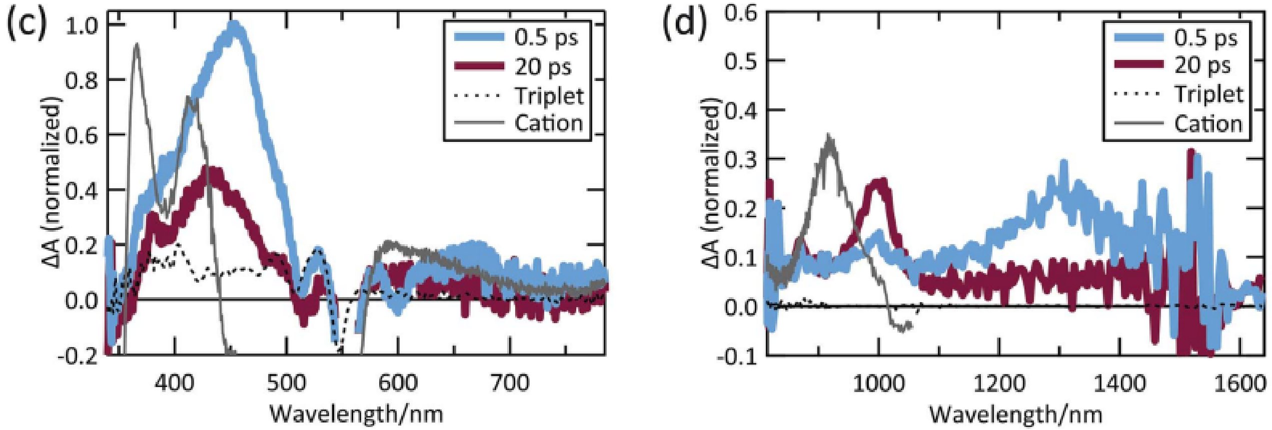


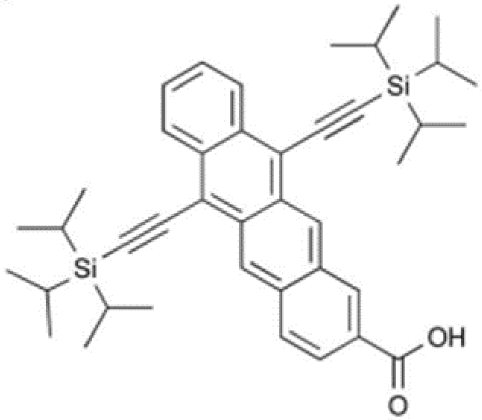


Pentacene on TiO_2

τ_{SF} ~ sub-ps

Low driving force





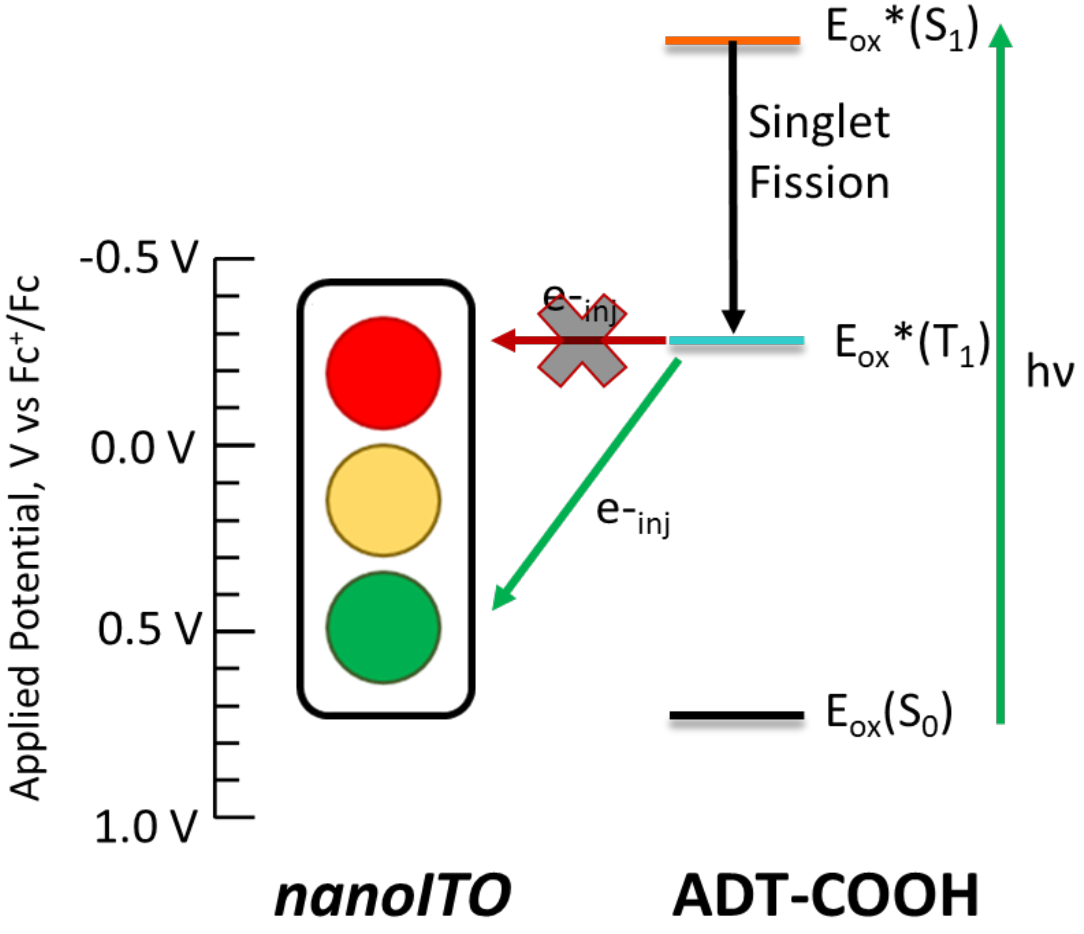
Tetracene on TiO_2

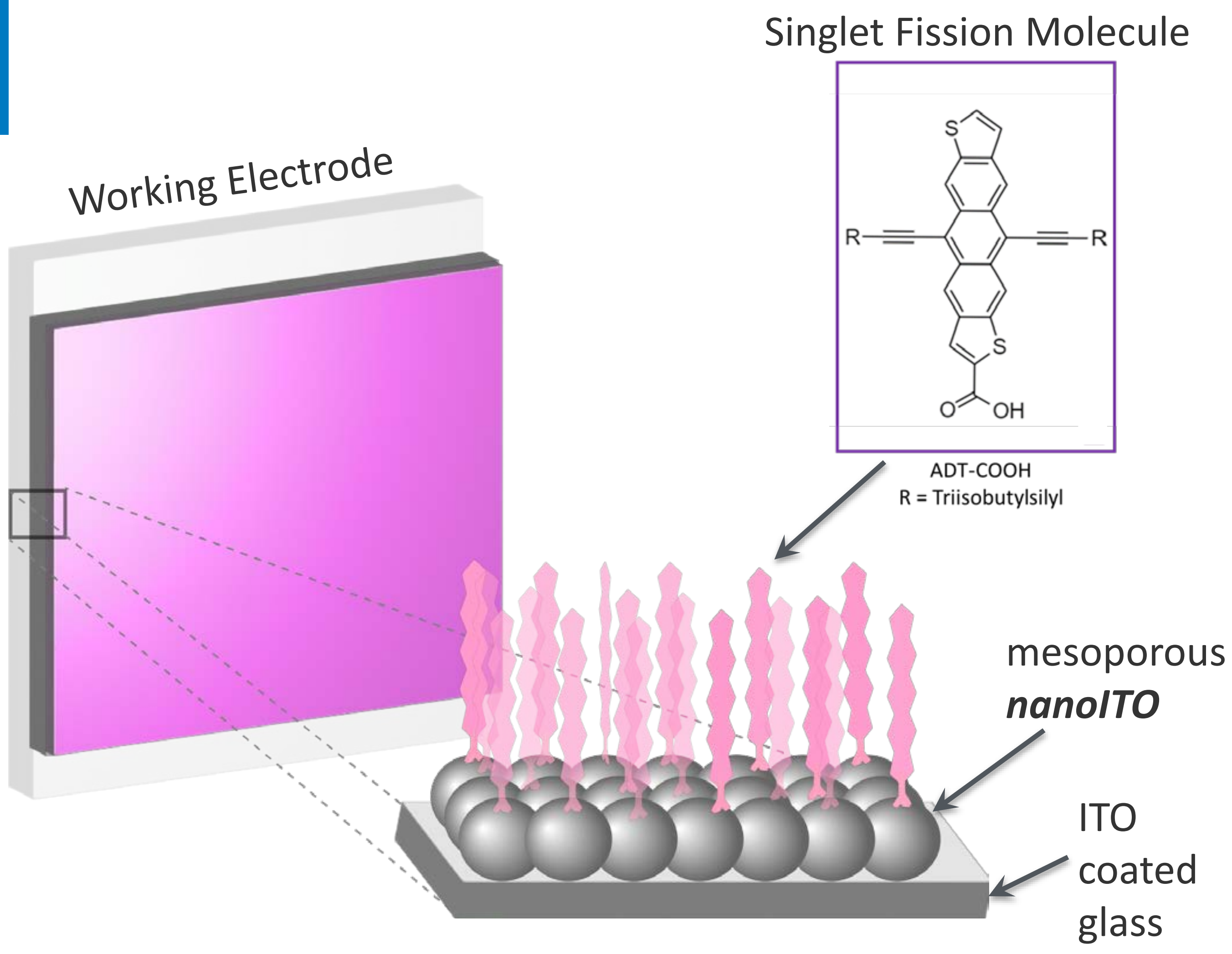
τ_{SF} ~ 40 ps

Singlet Injection

Pace, N.A.; Arias, D.H., *et.al.*, *Chem. Sci.*, **2018**, *9*, 3004.

Understanding Behavior of Singlet Fission-Borne Triplets





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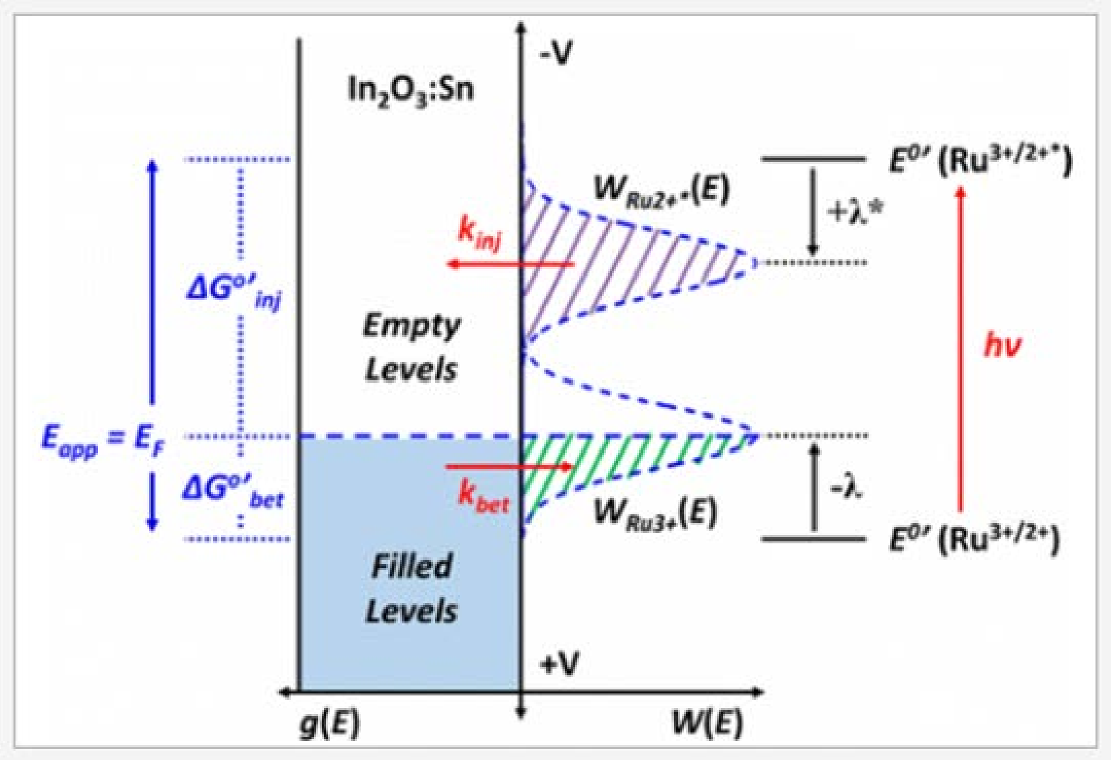
Controlling the driving force-nanoITO



J. Am. Chem. Soc. **2014**, 136, 45, 15869–15872.

Mesoporous indium tin oxide (*nanoITO*) is semi-metallic, allowing for direct control over the driving force

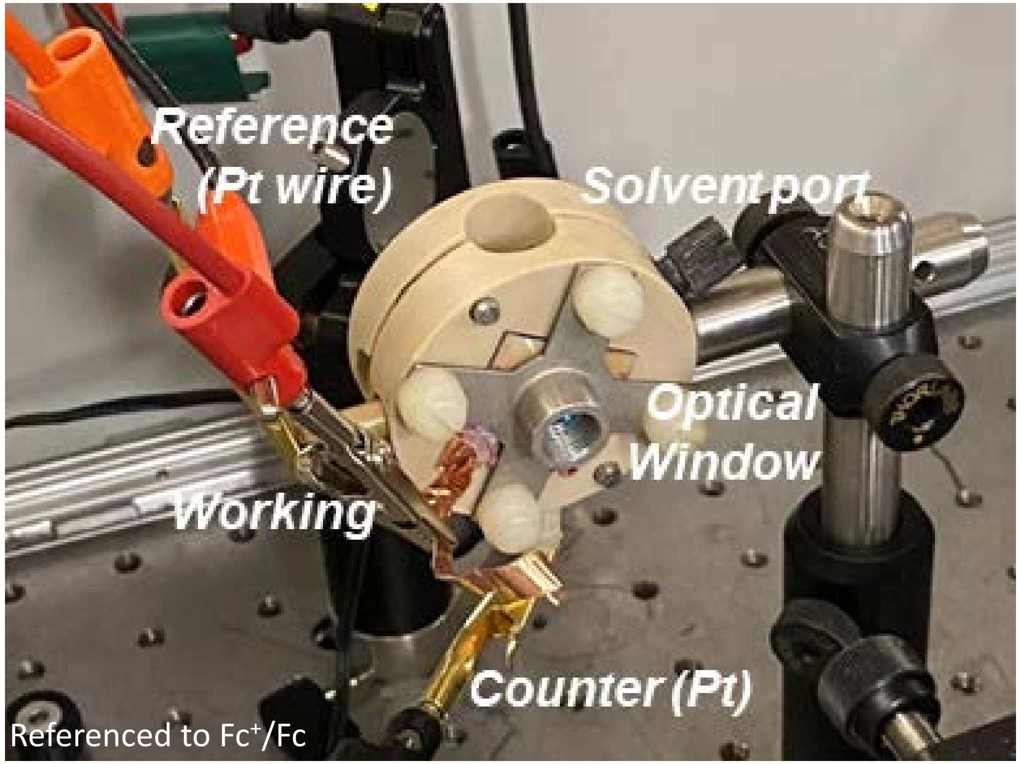
Not limited by conduction band edge, like in TiO_2

Previously done with $Ru(bpy)_3^{2+}$

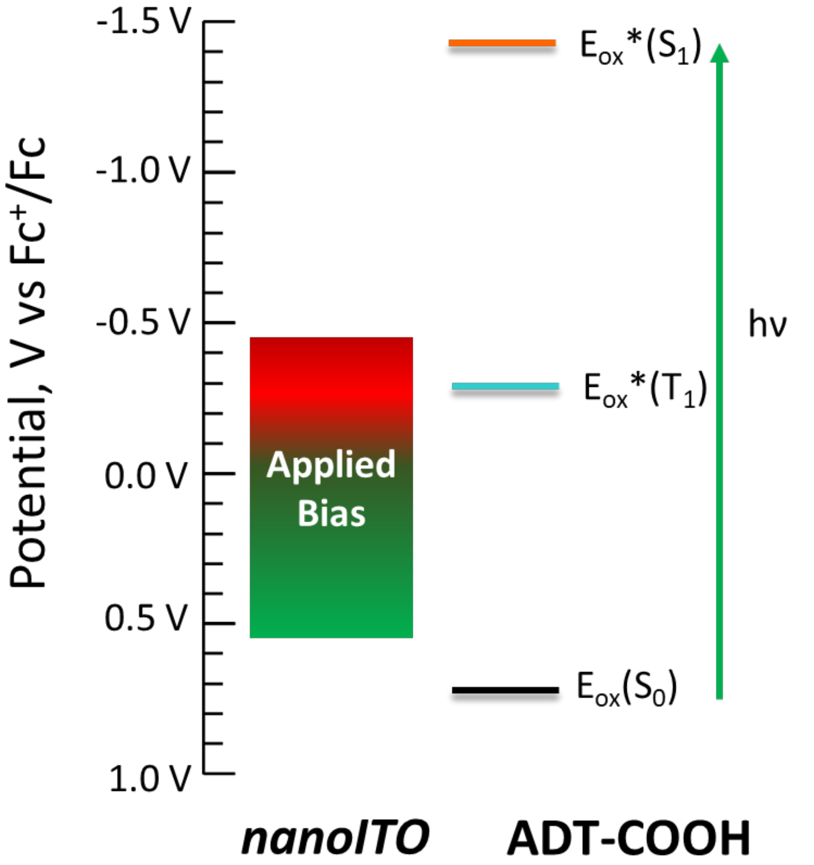
Applied Bias Transient Absorption

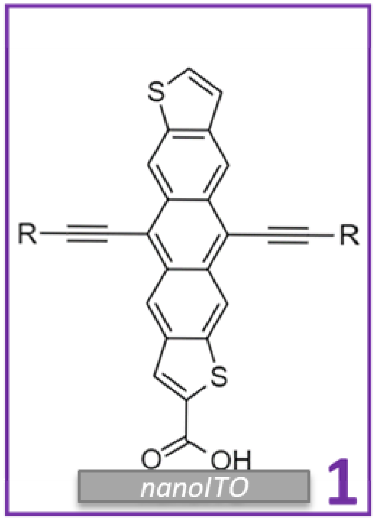
Can we observe triplet injection turn on?

What is the difference in electron injection behavior between singlet and triplet excited states?



Working electrode: *nanoITO*:**ADT-COOH** in 0.1 M $TBAPF_6$ in MeCN





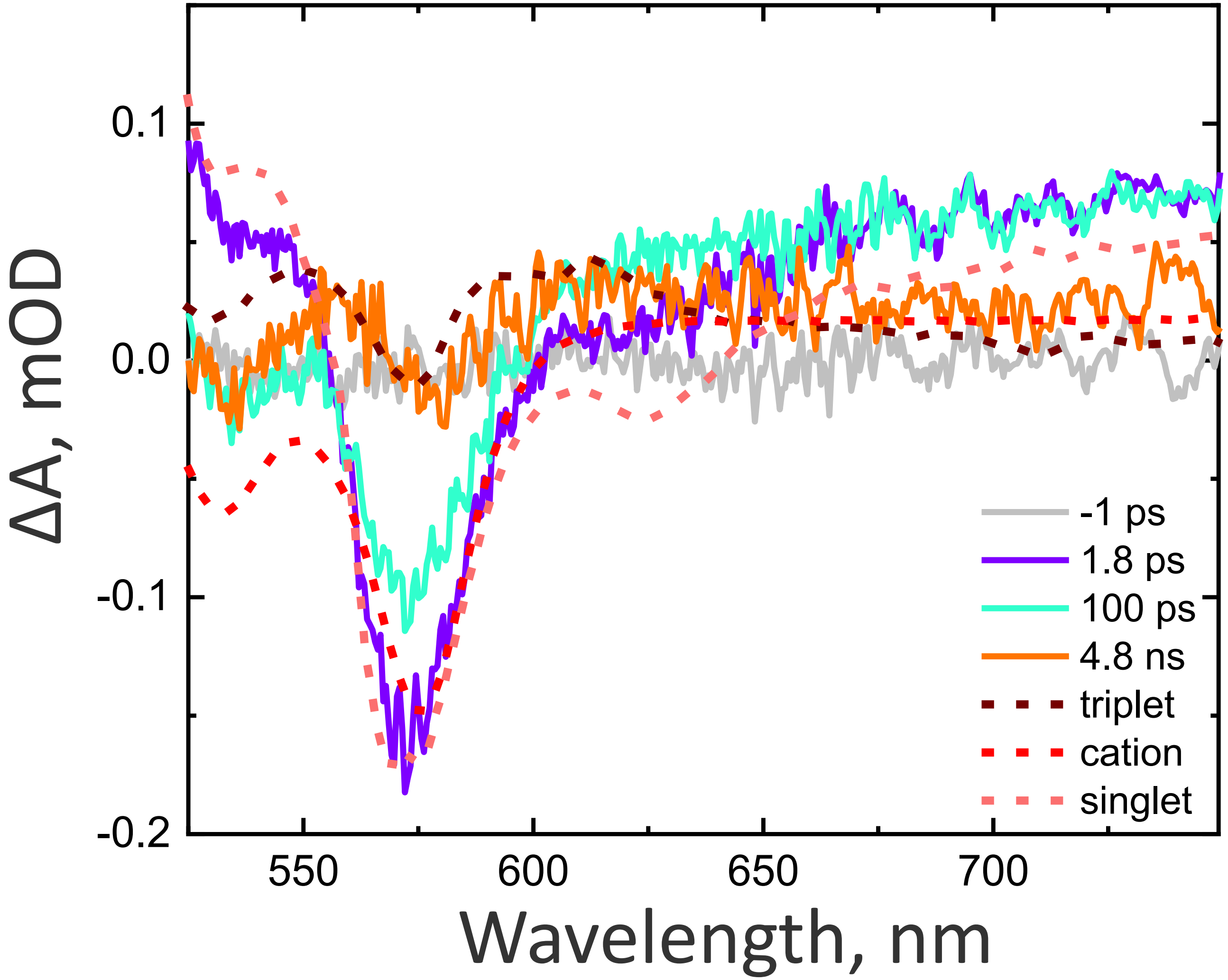
ADT-COOH
R = Triisobutylsilyl
$E(S_1)$ = 2.14 eV

Gish, M.K., Raulerson, E.K., Pekarek, R.T., Greenaway, A.L., Thorley, K.J., Neale, N.R., Anthony, J.E., Johnson, J.C., *Chem. Sci.*, **2021**, *12,* 11146-11156.

Overlapping features complicate spectra

λ_{pump} = 500 nm (60 nJ/pulse)

Dry *nanoITO*:**ADT-COOH** in N_2 atmosphere



Component spectra:

- *Singlet*: fsTA of **ADT-COOH**
- *Triplet*: nsTA of Anthracene sensitization of **ADT-COOH**
- *Cation*: Spectroelectrochemistry (UV-Vis)

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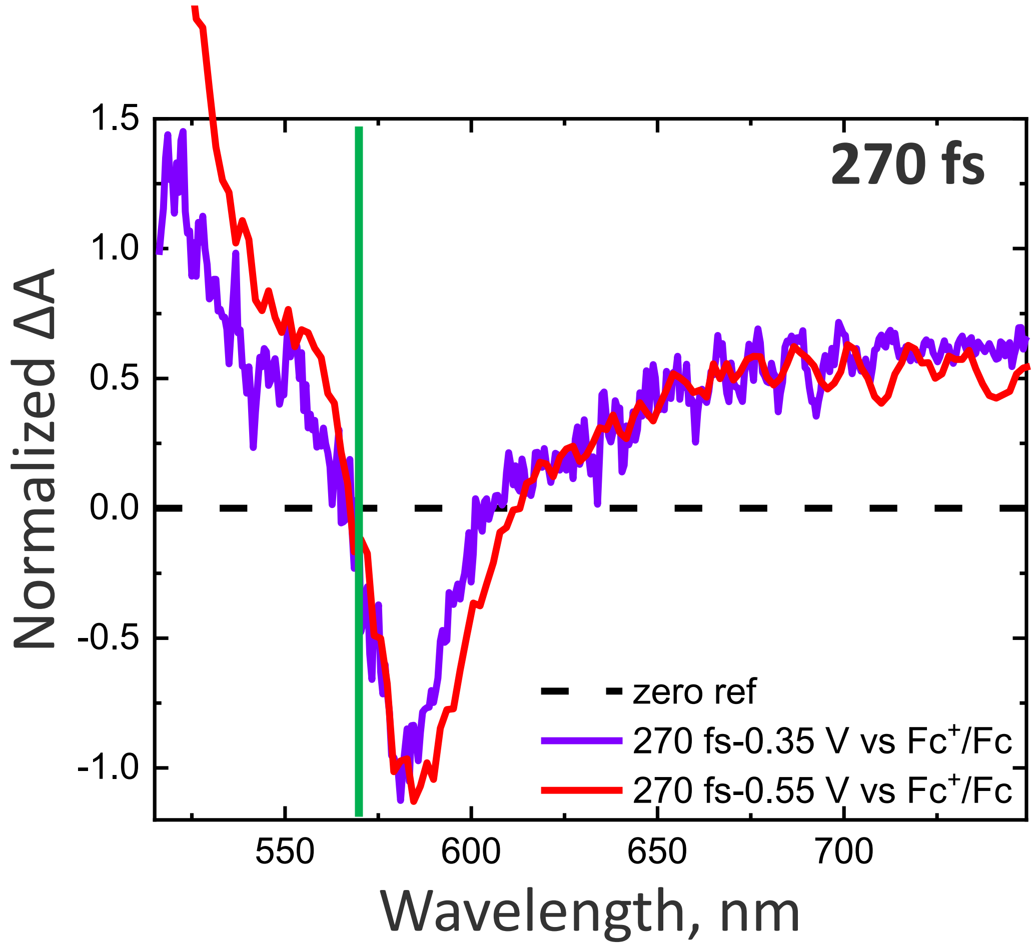
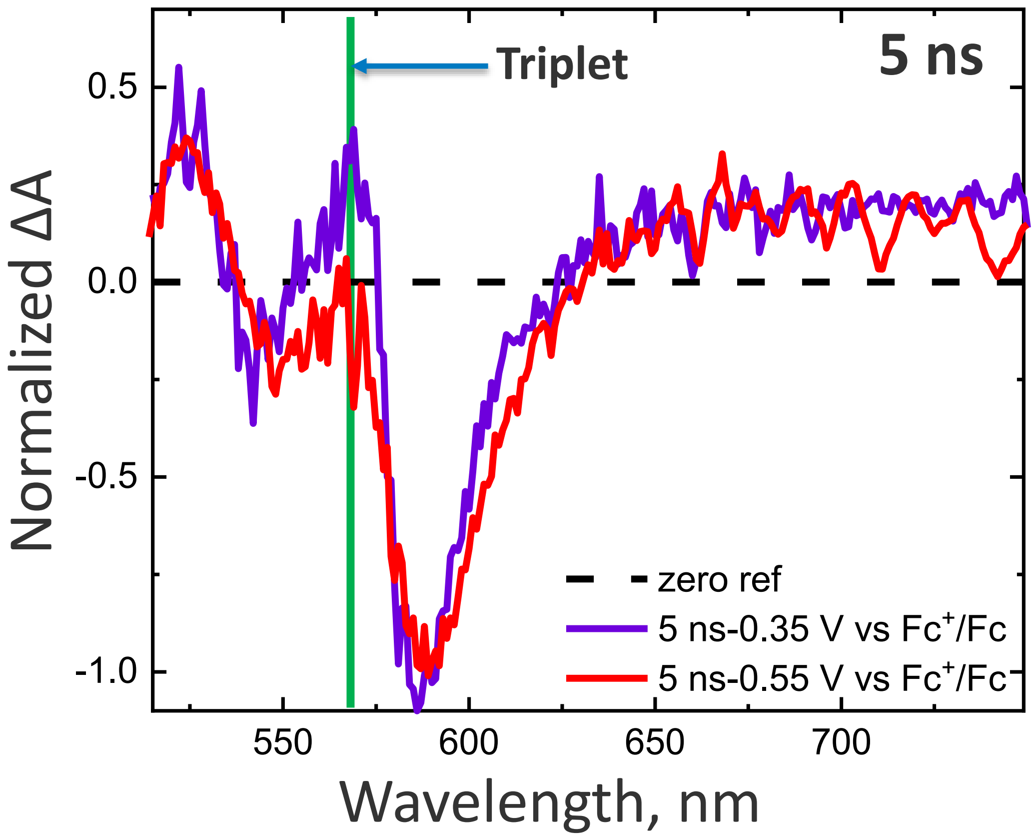
Triplet decays faster with increasing bias

Purple : $\Delta G(T_1)$ = -0.68 eV
Red: $\Delta G(T_1)$ = -0.88 eV

λ_{pump} = 500 nm (60 nJ/pulse)
nanoITO:**ADT-COOH**
in 0.1 M $TBAPF_6$ in MeCN





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Order of magnitude increase in triplet rate

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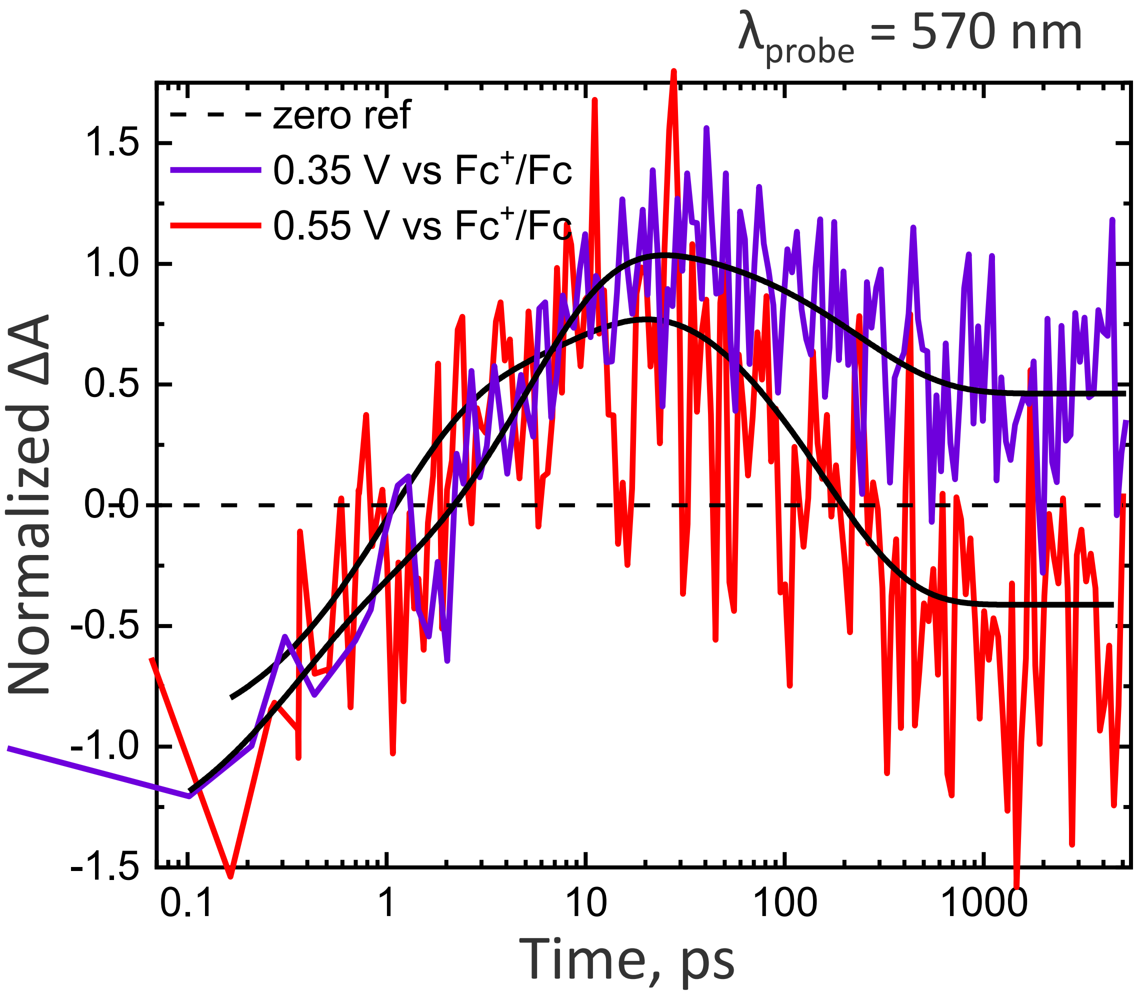

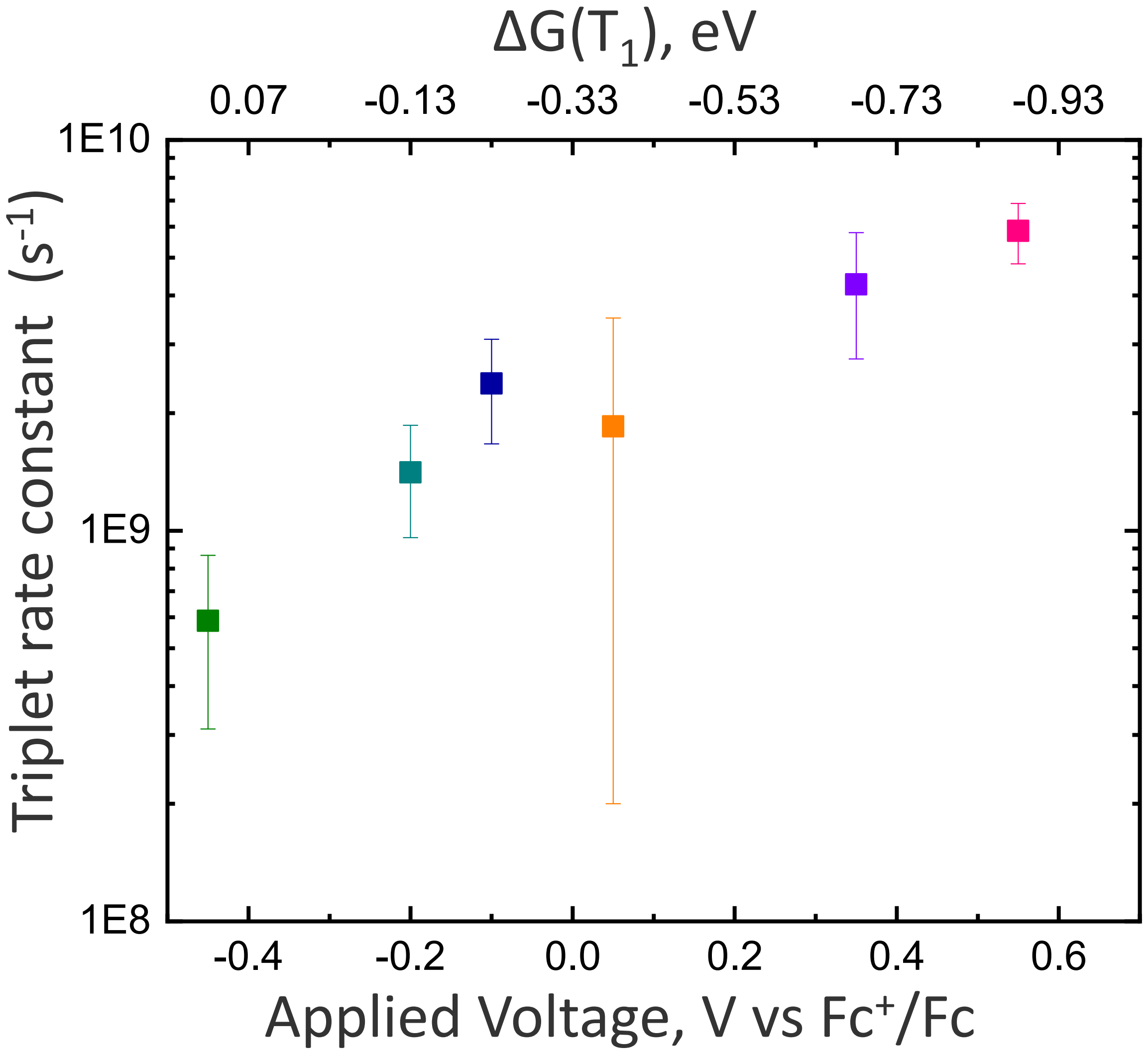

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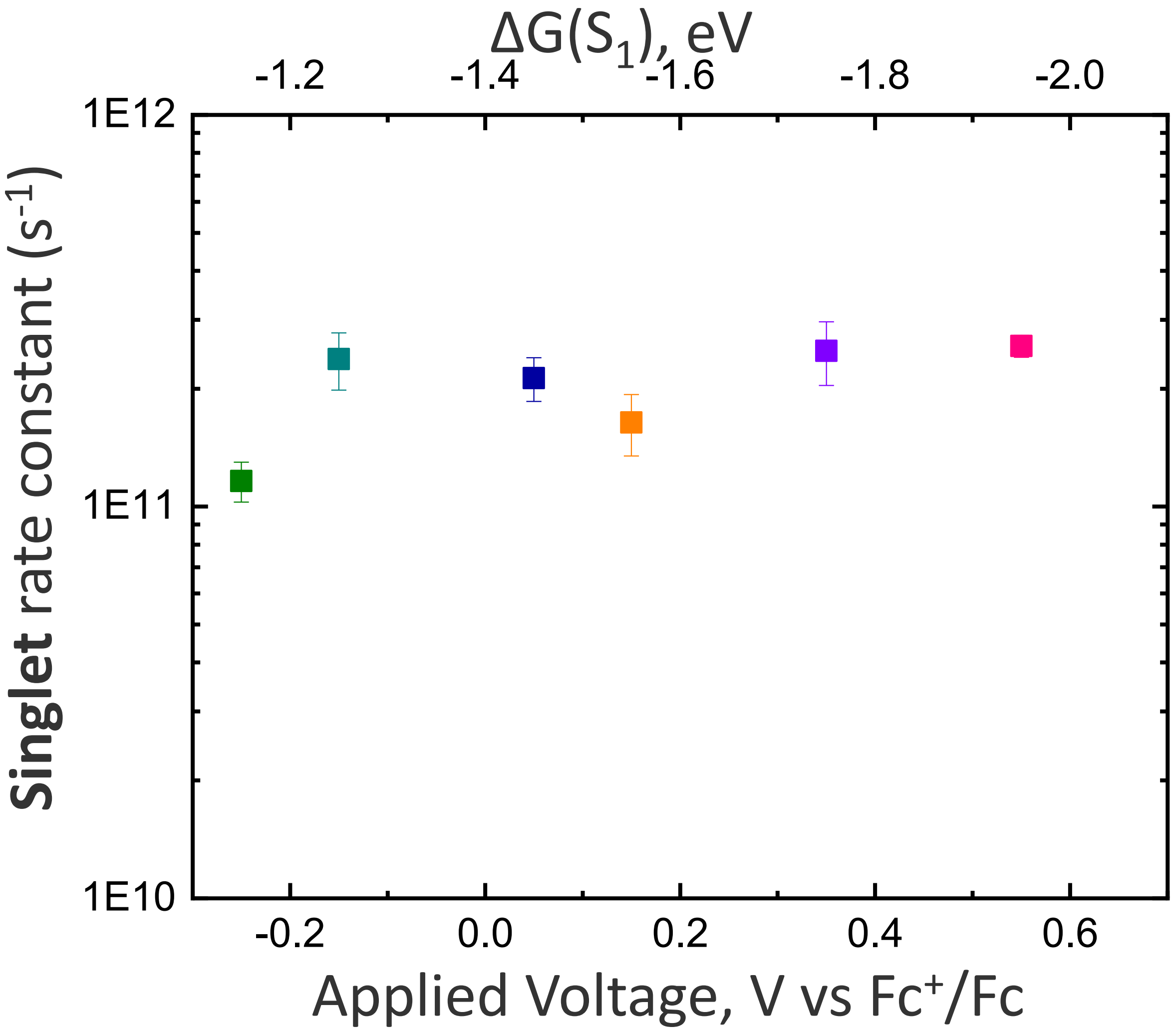
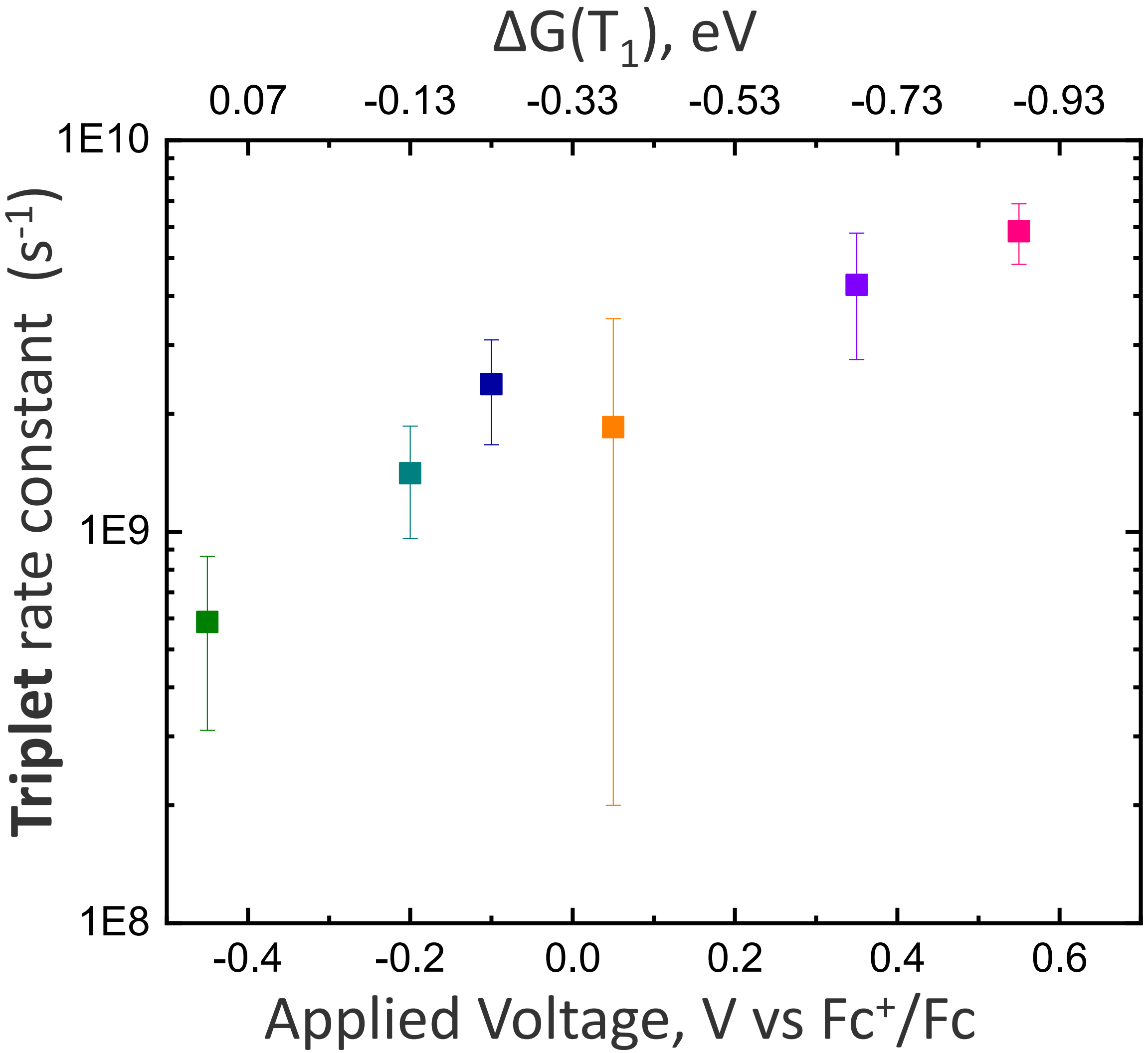
Singlet exhibits no change over same range

λ_{pump} = 500 nm (60 nJ/pulse)





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Adapting Marcus Theory

λ_{pump} = 500 nm (60 nJ/pulse)

Marcus Equation assumes 1 donor and 1 acceptor:

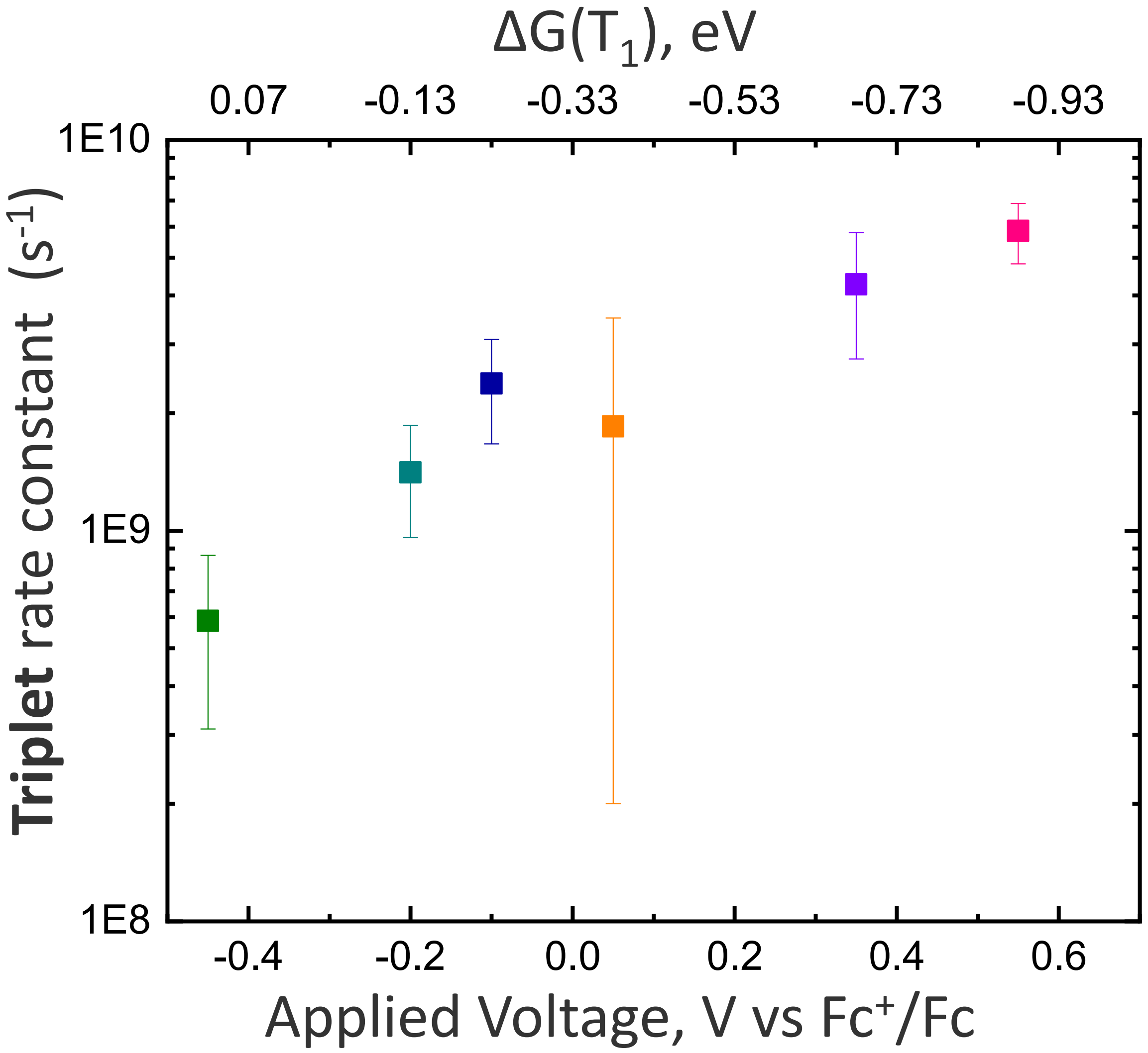
$$k_{ET} = \frac{2\pi}{\hbar}|H_{DA}|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(\lambda+\Delta G)^2}{4\lambda k_B T}\right)$$

nanoITO **is a** **distribution** **of acceptor levels**

$$\frac{k_{inj}}{k_{inj}^{max}} = \frac{1}{2}\left[1 - \text{erf}\left(\frac{\lambda+\Delta G}{\sqrt{4\lambda k_B T}}\right)\right]$$

where

$$k_{inj}^{max} = \frac{2\pi}{\hbar} H_{DA}{}^2 g$$



J. Am. Chem. Soc. 2014, 136, 45, 15869–15872.
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Adapting Marcus Theory

$H_{DA}(S_1) = 3.5$ meV
$H_{DA}(T_1) = 0.53$ meV

$\lambda_{pump} = 500$ nm (60 nJ/pulse)

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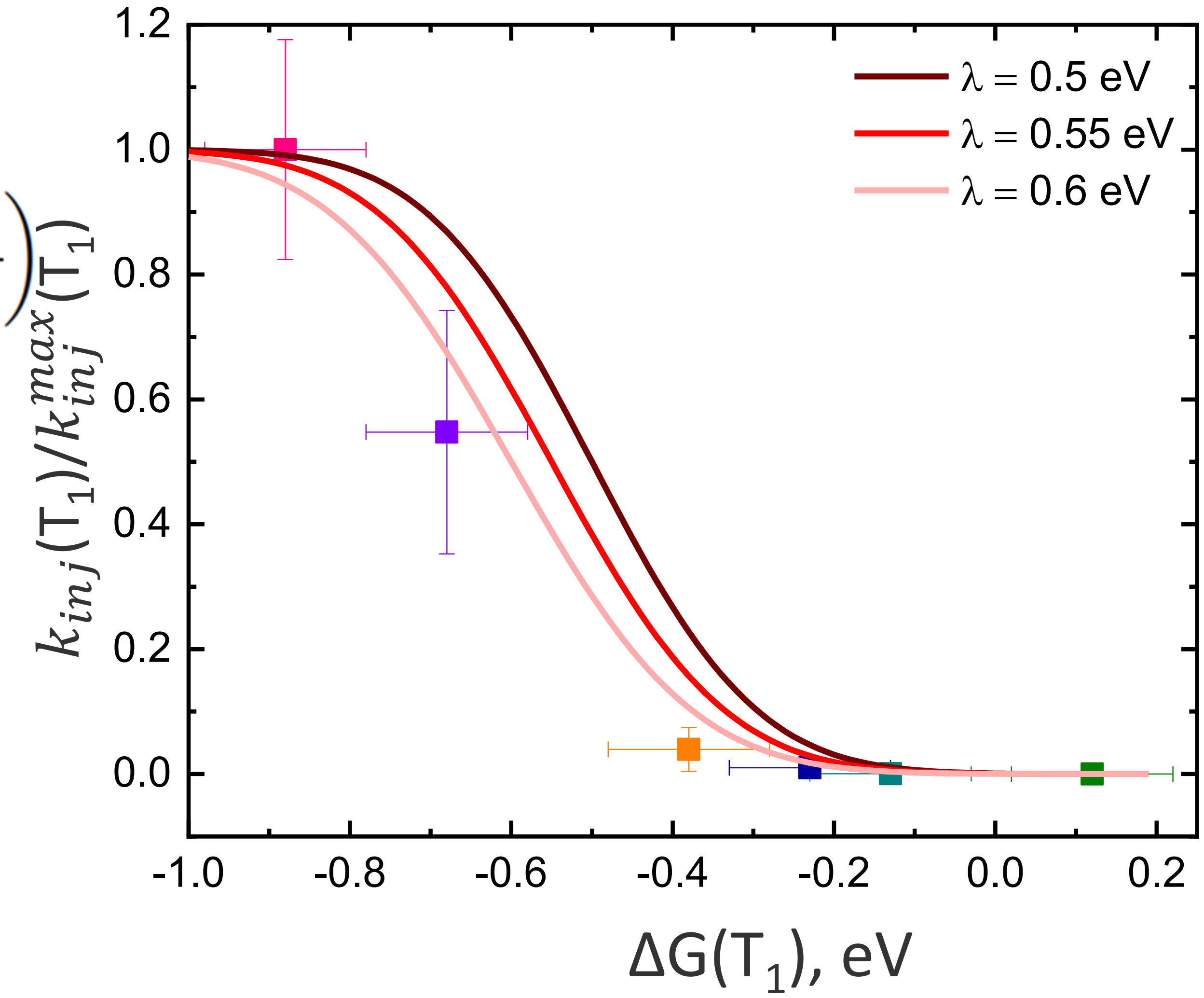

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No traditional inverted regime

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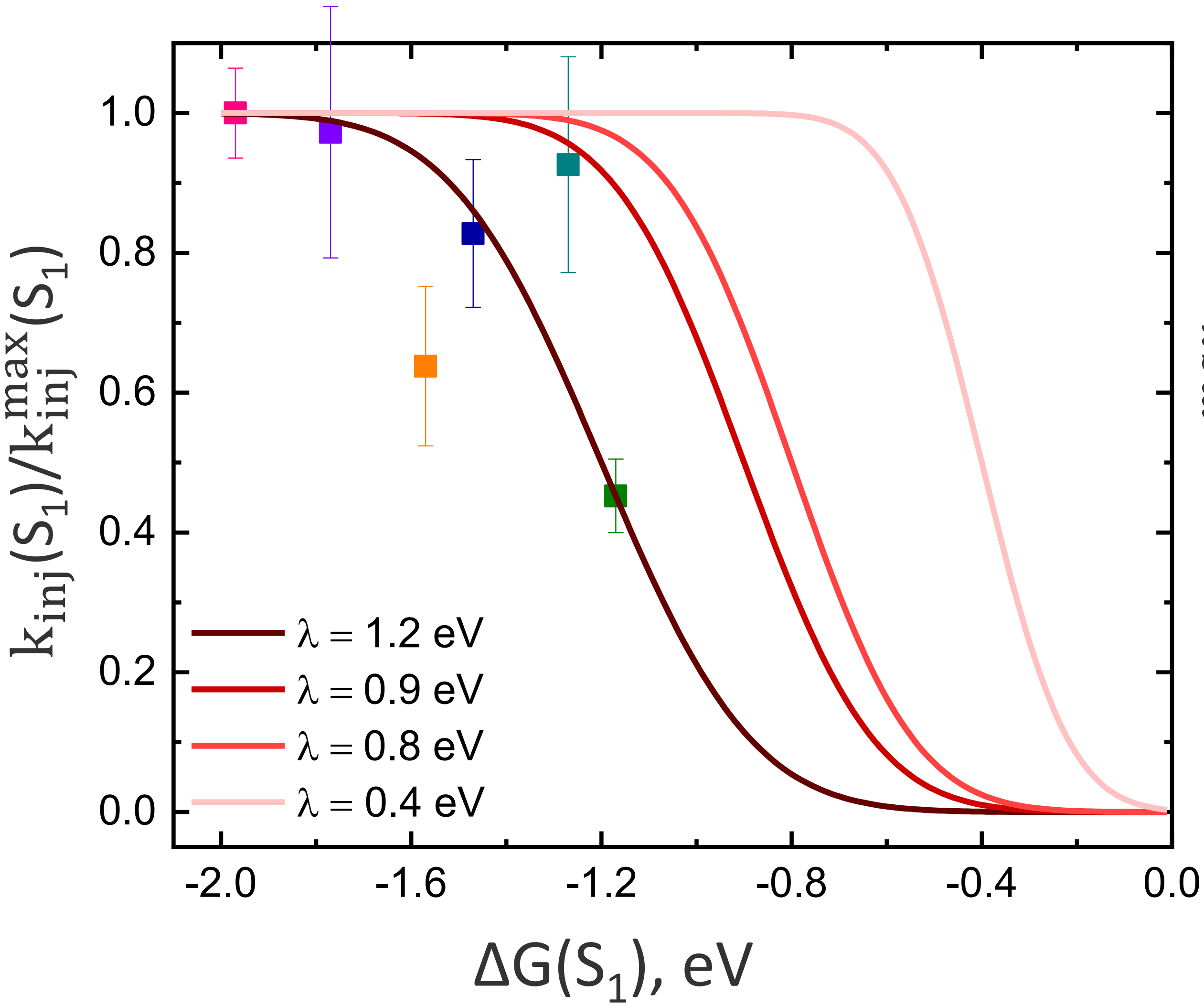

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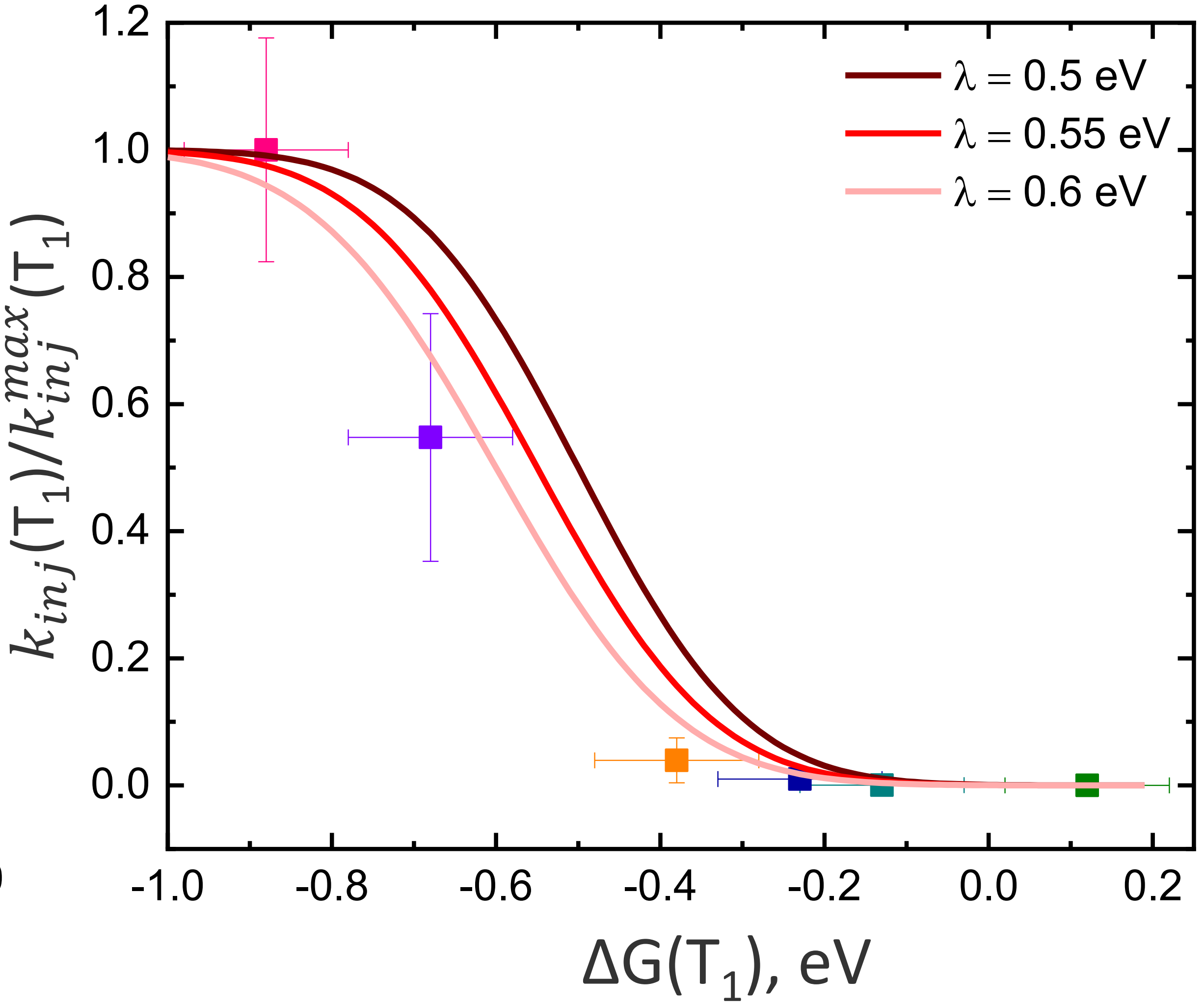

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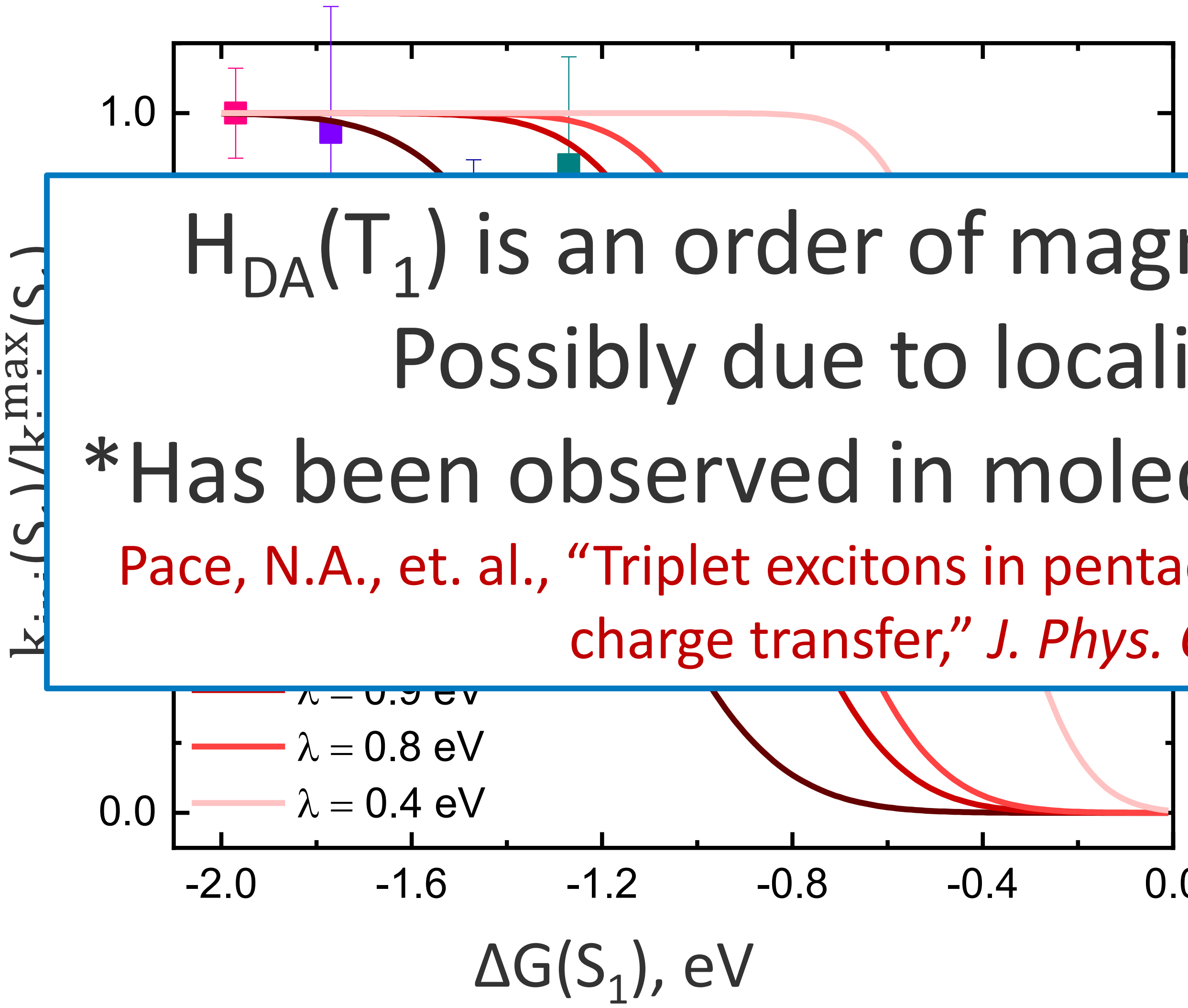

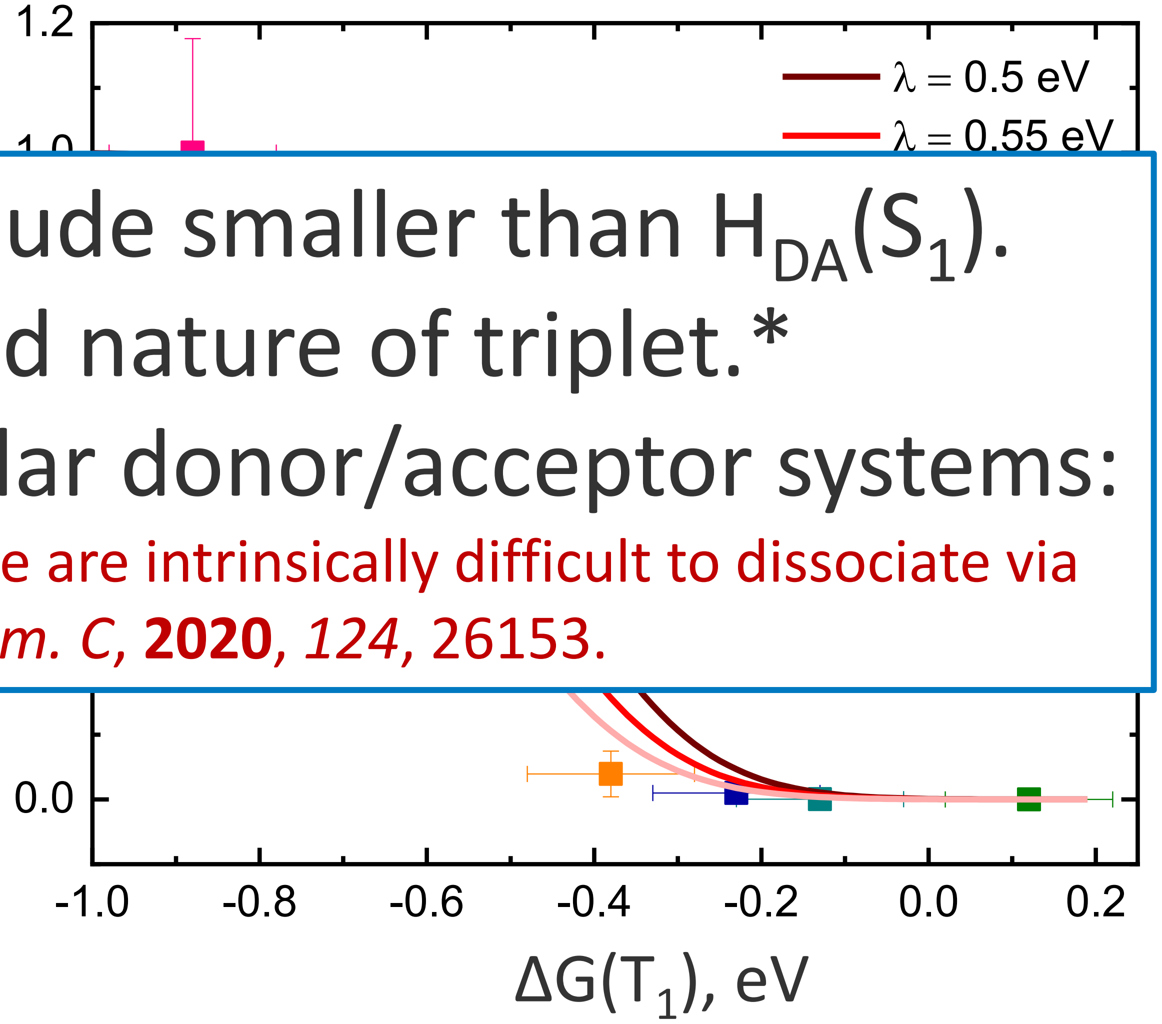

$H_{DA}(T_1)$ is an order of magnitude smaller than $H_{DA}(S_1)$. Possibly due to localized nature of triplet.*

*Has been observed in molecular donor/acceptor systems:

Pace, N.A., et. al., "Triplet excitons in pentacene are intrinsically difficult to dissociate via charge transfer," *J. Phys. Chem. C*, **2020**, *124*, 26153.

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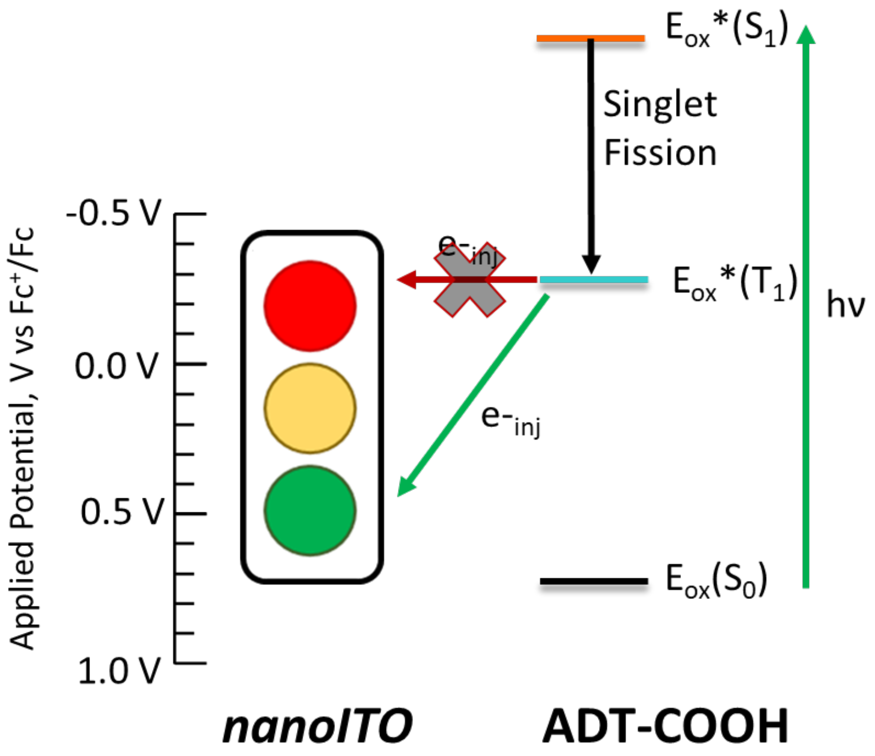
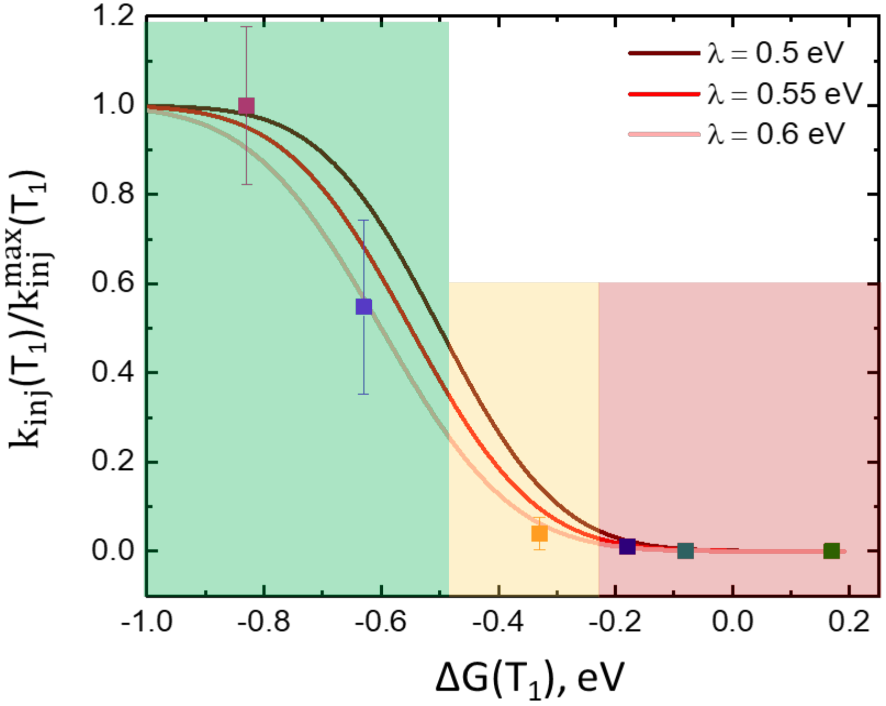
Summary





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Acknowledgements


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