Spin-triplet excited states in organic semiconductors

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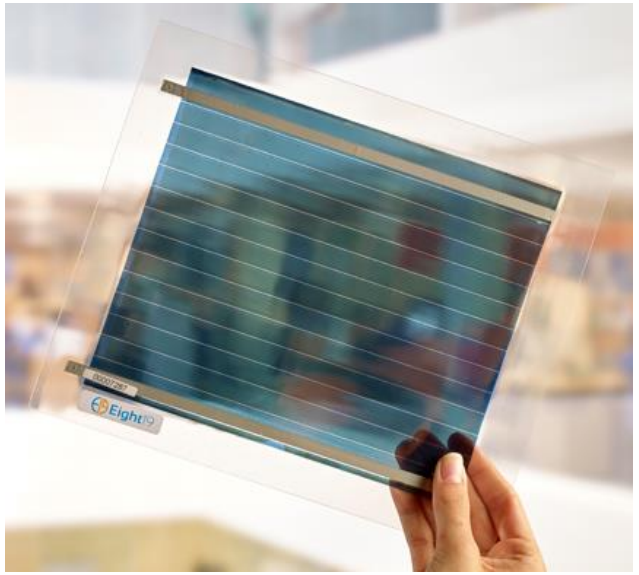
LINKÖPING UNIVERSITY

Organic semiconductors

Samsung Galaxy Z Fold5, flexible OLED screen



A low temperature screen-printed organic PV module. Cheap to make, transparent, bendable.

- Semiconductors made from primarily carbon and hydrogen atoms
- Disordered, relatively impure materials. Yet work surprisingly well in optoelectronic applications

Organics are excitonic semiconductors

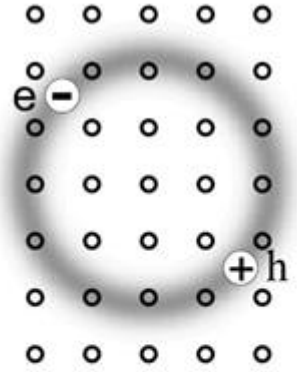
$$E_c = \frac{e^2}{4\pi\varepsilon_0\varepsilon_R r}$$

Need to overcome the exciton binding energy in organics to generate free charge carriers!

Organic

Frenkel exciton

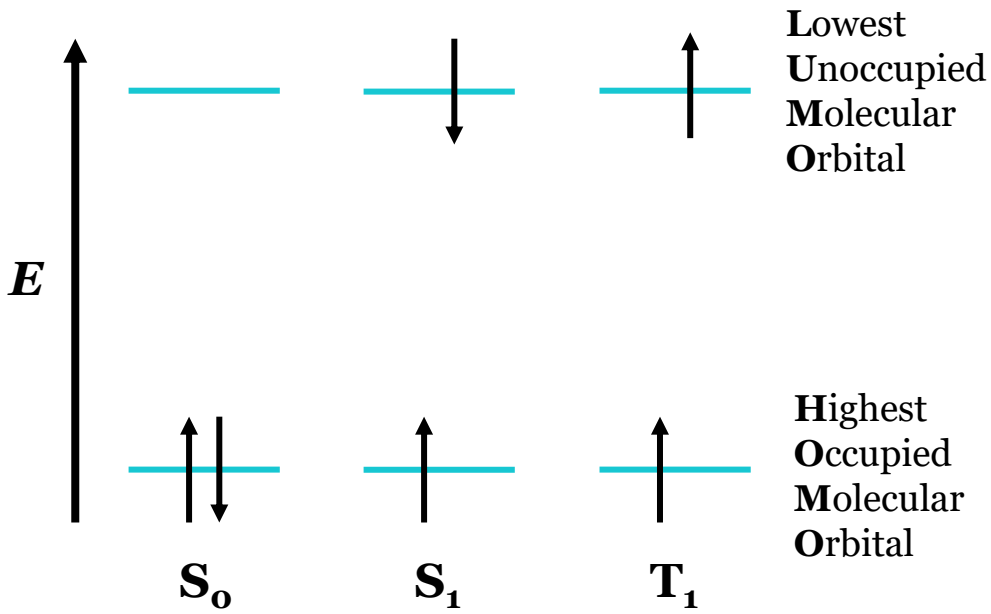
Inorganic (Si)



Wannier exciton

Dielectric constant (ε_R):	2 - 4	11.7 (for Si)
Exciton binding energy:	0.1 – 1 eV	15 meV
Exciton radius:	1 nm (localized on single molecule)	10 nm (effectively free carriers at RT)

Exciton spin



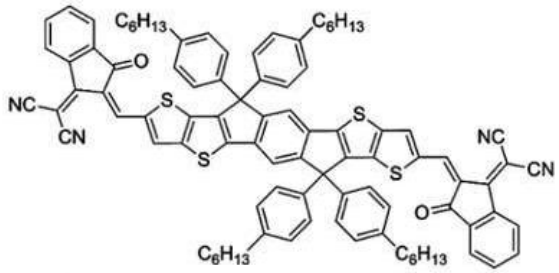
$\Delta E_{ST} = 2J$

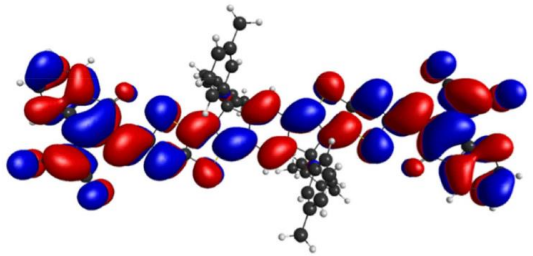
(J = electron exchange energy)

$$J = \iint \varphi_H(r_1)\varphi_L(r_2)\left(\frac{e^2}{4\pi\varepsilon_0(r_1 - r_2)}\right)\varphi_H(r_2)\varphi_L(r_1)\, dr_1 dr_2$$

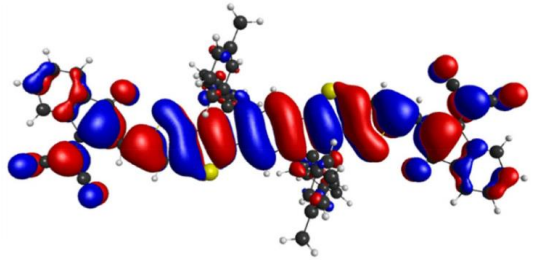
ΔE_{ST} ~ 0.6-1 eV in organic conjugated polymers

ITIC





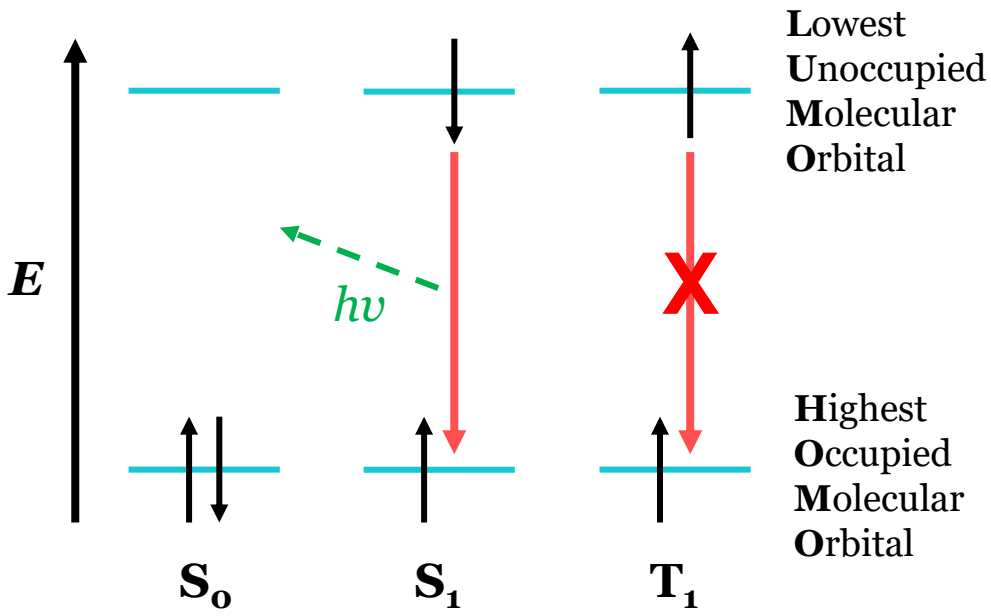
LUMO



HOMO

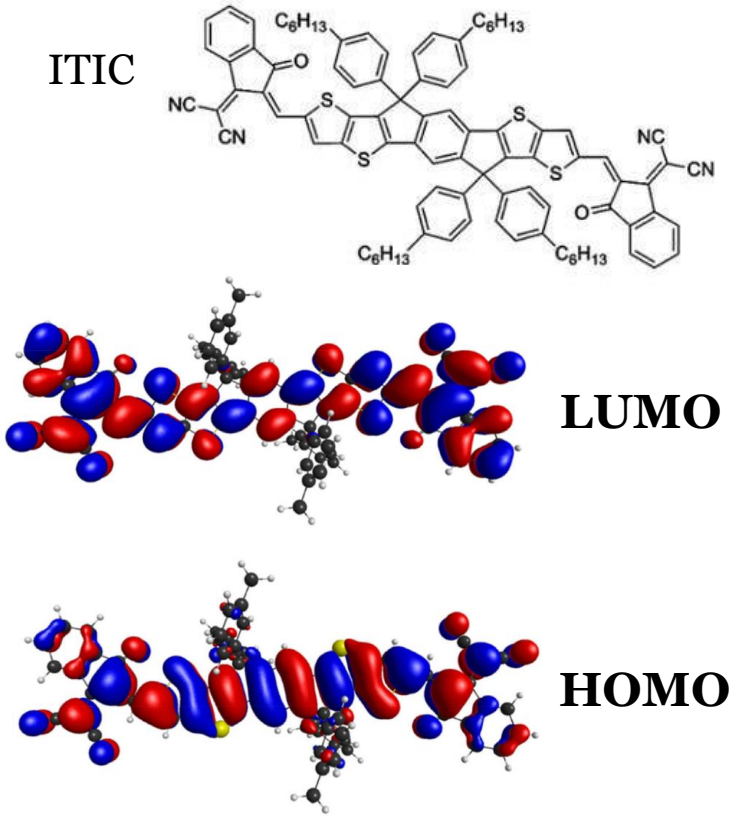
S. M. Swick, et al., *ChemPhysChem*, 2019, **20**, 2608–2626

Exciton spin



- Spin triplet states are dark states
- Radiative recombination of triplets is formally spin-forbidden

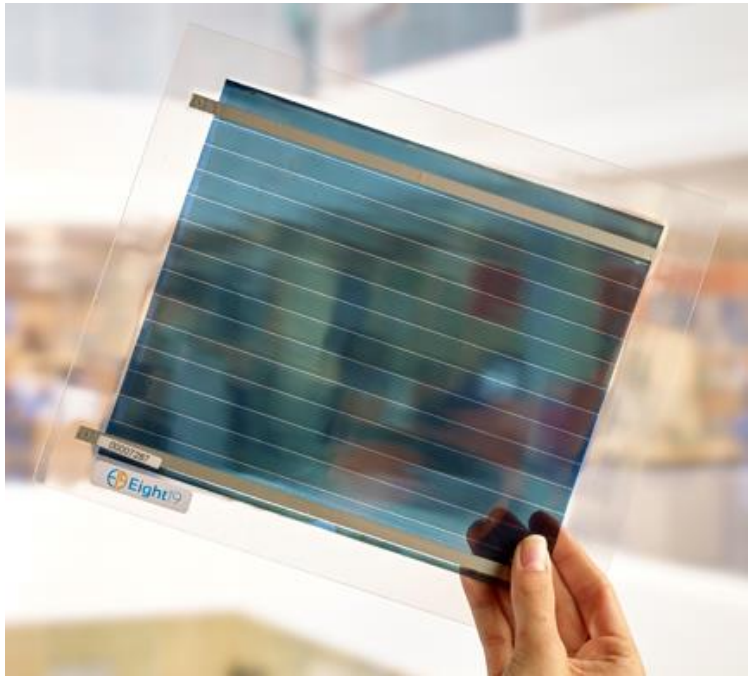
ΔE_{ST} ~ 0.6-1 eV in organic conjugated polymers



S. M. Swick, et al., *ChemPhysChem*, 2019, **20**, 2608–2626

Organic photovoltaics – on the cusp of applications

- Organic photovoltaics (PV) now have a power conversion efficiency of >21%
- Why only 21%? Silicon and perovskite PV are >25%
- Could triplet excitons be involved in this somehow?



A low temperature screen-printed OPV module. Cheap to make, transparent, bendable.

Voltage loss in solar cells

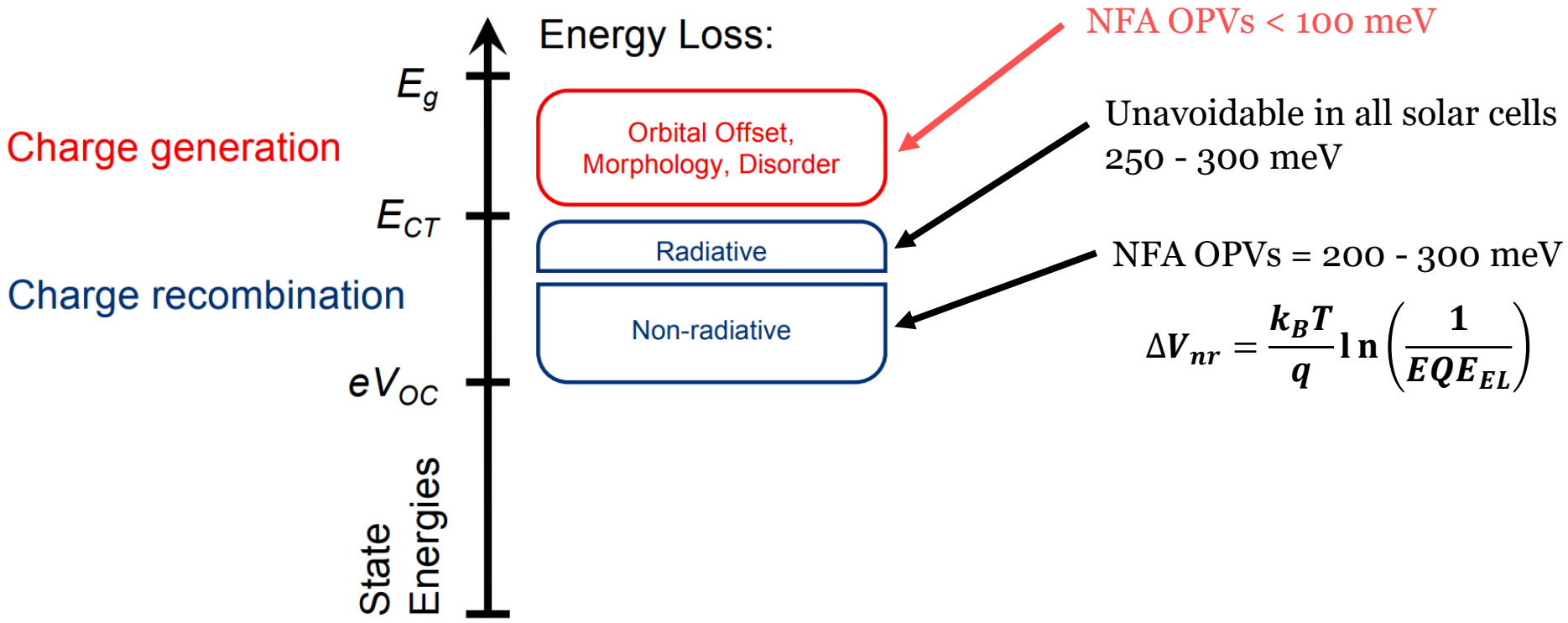


*Figure adapted from S. M. Menke et al., Joule, 2017, **1**, 1–11*

Voltage loss in solar cells

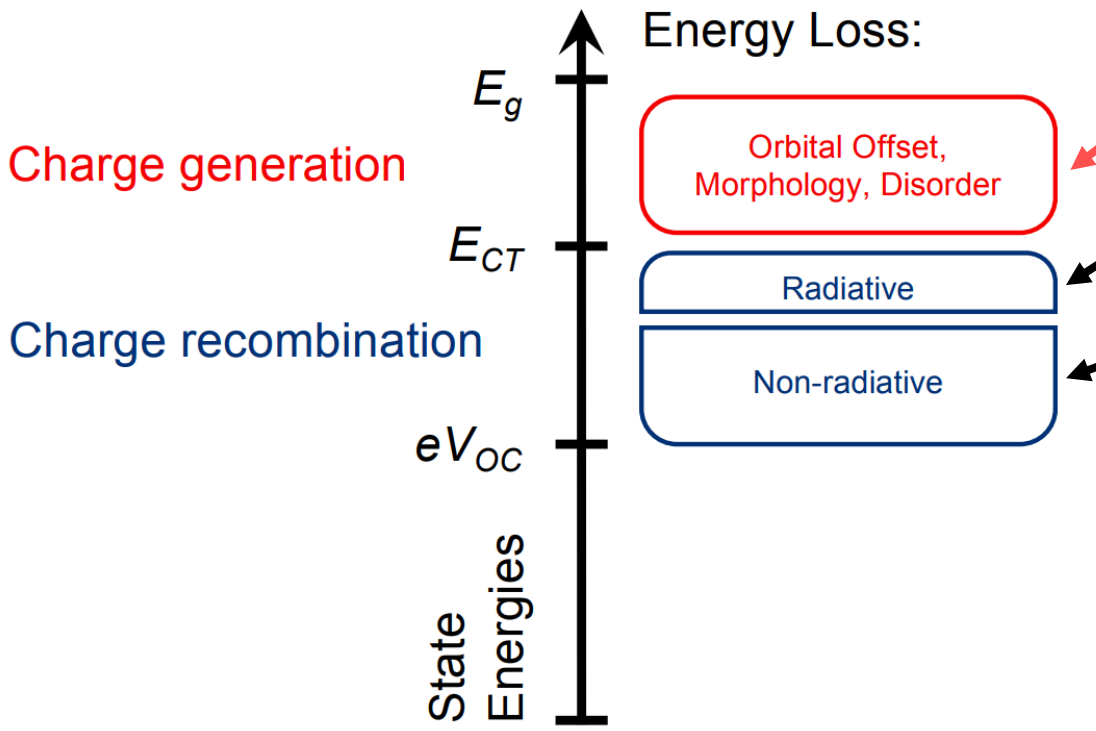


*Figure adapted from S. M. Menke et al., Joule, 2017, **1**, 1–11*

NFA OPVs < 100 meV

Unavoidable in all solar cells
250 - 300 meV

NFA OPVs = 200 - 300 meV

$$\Delta V_{nr} = \frac{k_B T}{q} \ln\left(\frac{1}{EQE_{EL}}\right)$$

Total voltage loss

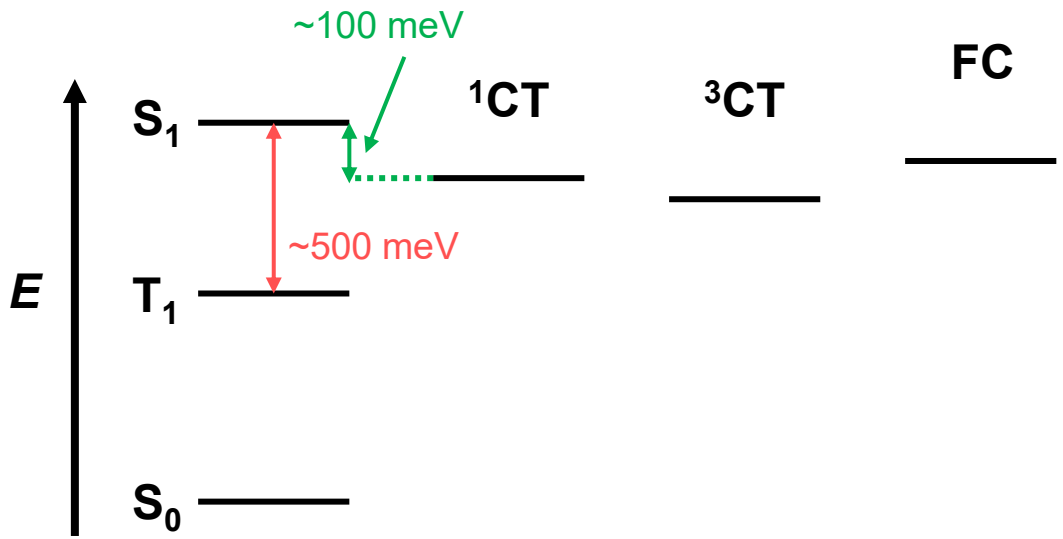
GaAs = 320 mV ($\Delta V_{nr} = 40\ mV$)

c-Si = 380 mV ($\Delta V_{nr} = 120\ mV$)

Perovskite = 350 - 500 mV ($\Delta V_{nr} = 60\ mV$)

NFA OPVs = 500 - 600 mV ($\Delta V_{nr} = 200\ mV$)

Thermodynamics favours triplet formation in OPVs



- In low offset non-fullerene acceptor systems, the NFA T_1 state will always be lower in energy than the charge transfer states
- Dissociation and reformation of CT states is an efficient spin mixing mechanism
- It is difficult to prevent recombination to triplet excitons in organic solar cells

Why does spin matter in OPVs?

$$\Delta V_{nr} = \frac{k_B T}{q} \ln\left(\frac{1}{EQE_{EL}}\right)$$

Why does spin matter in OPVs?

$$\Delta V_{nr} = \frac{k_B T}{q} \ln\left(\frac{1}{EQE_{EL}}\right)$$

Fraction of recombination events that can result in photon emission i.e. spin-singlet states

$$EQE_{EL} = \gamma \Phi_{PL} \chi \eta_{out}$$

Charge balance in device

Photoluminescence quantum efficiency (of singlet states)

Light out-coupling efficiency

Why does spin matter in OPVs?

$$\Delta V_{nr} = \frac{k_B T}{q} \ln\left(\frac{1}{EQE_{EL}}\right)$$

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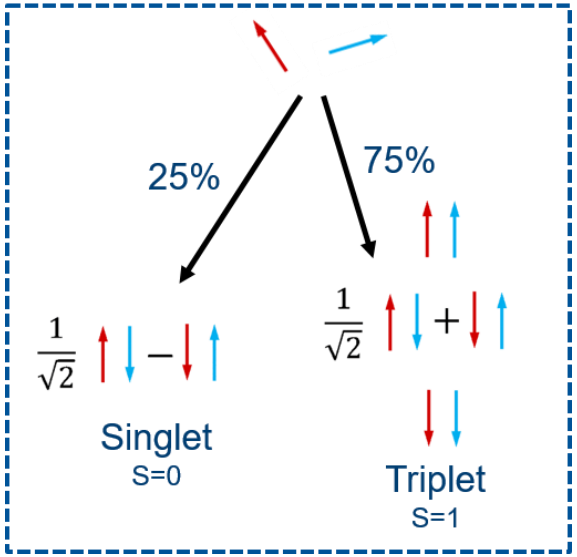
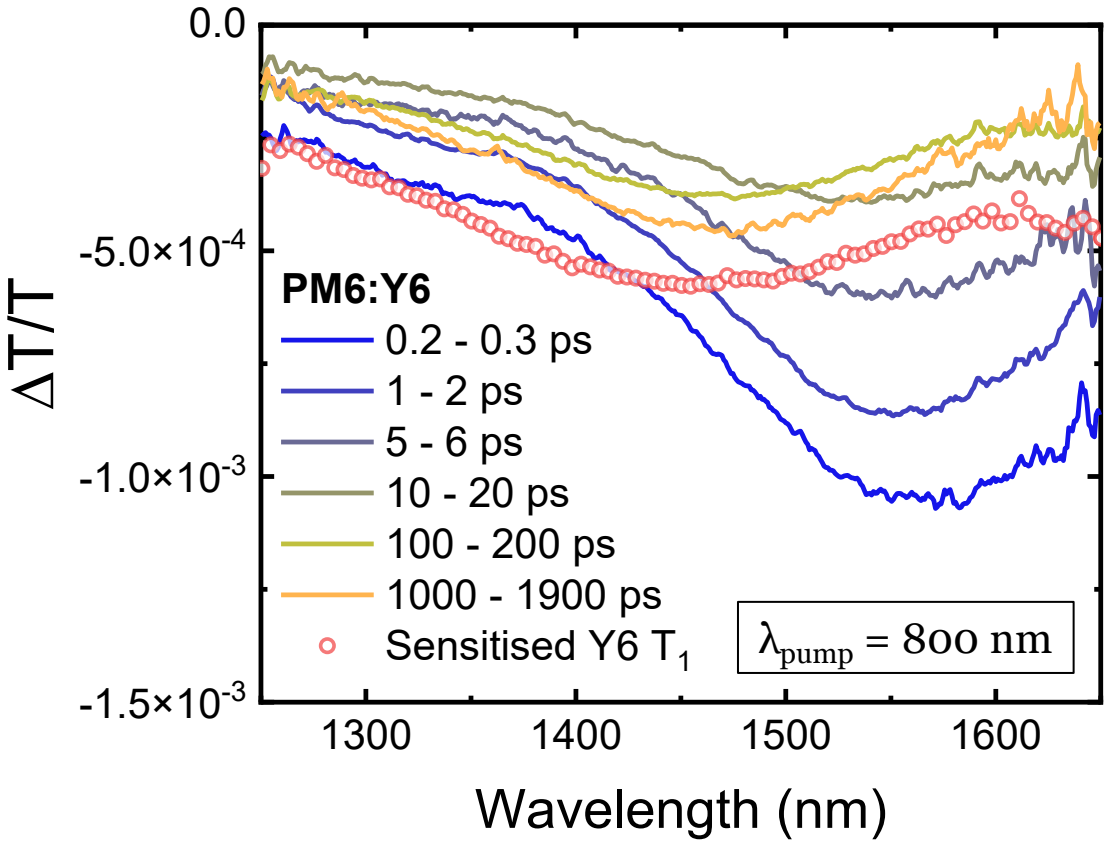
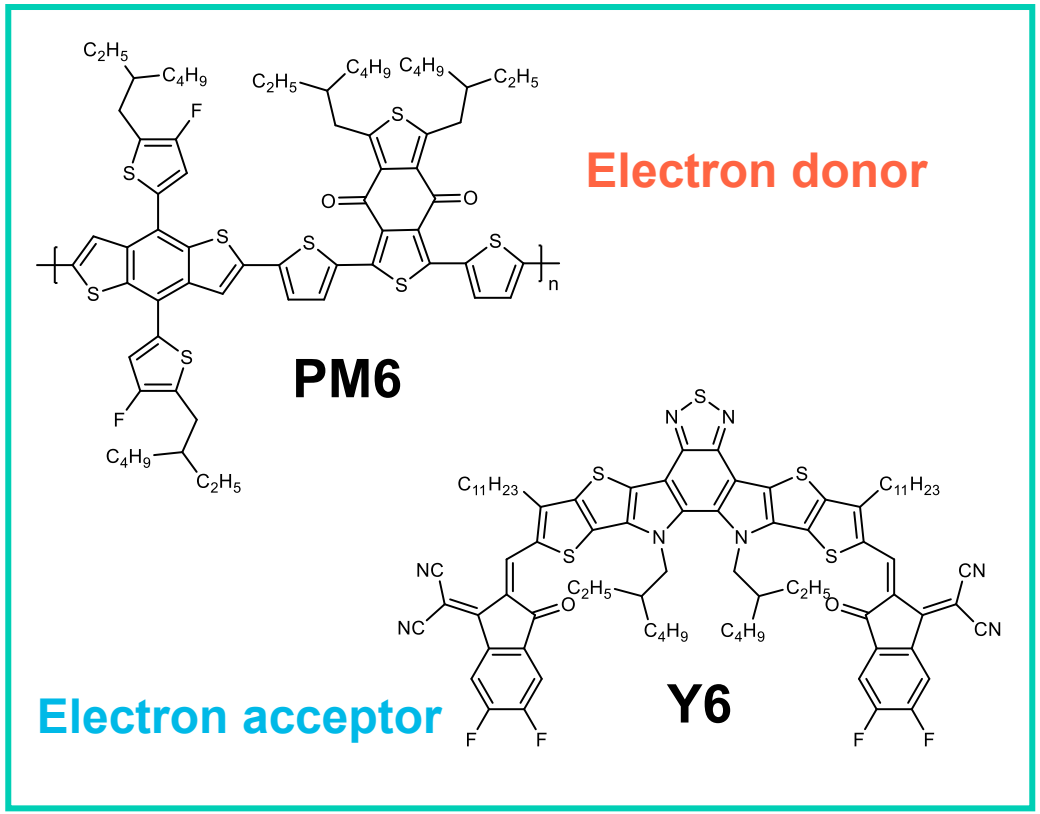
Photoluminescence quantum efficiency (of singlet states)



- Limited scope to increase PLQE in narrow band gap organics due to energy gap law
- If we want to improve the EQE_{EL}, we need to target triplet recombination (cf. OLEDs)

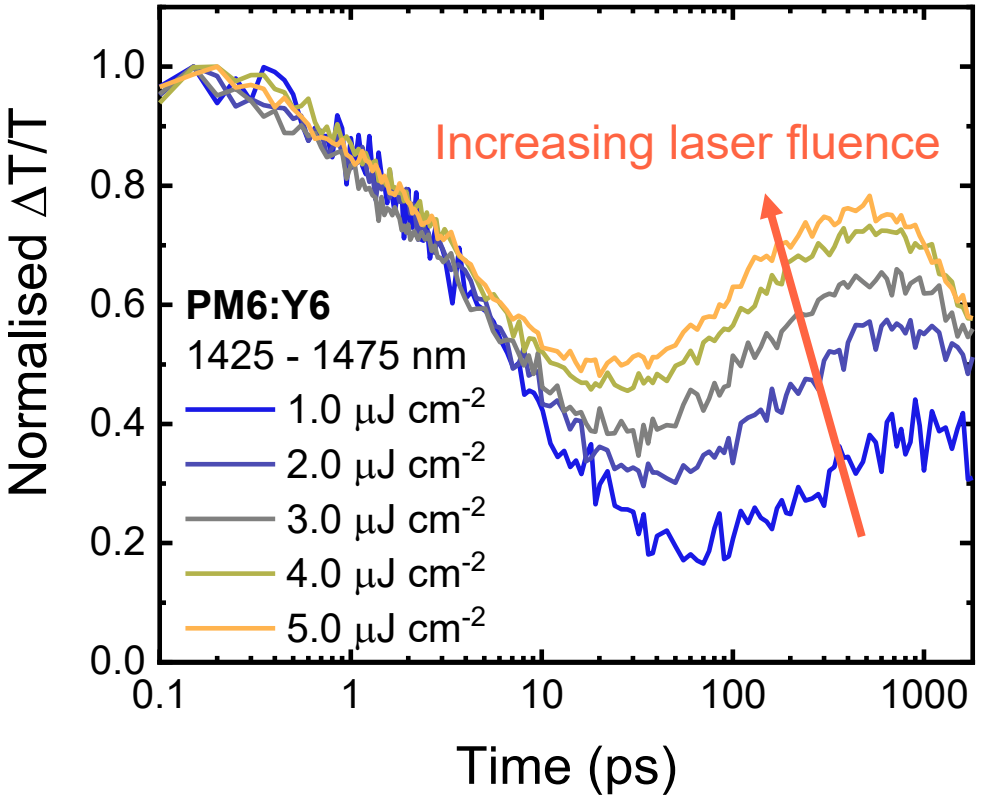
Probing triplet recombination with TAS

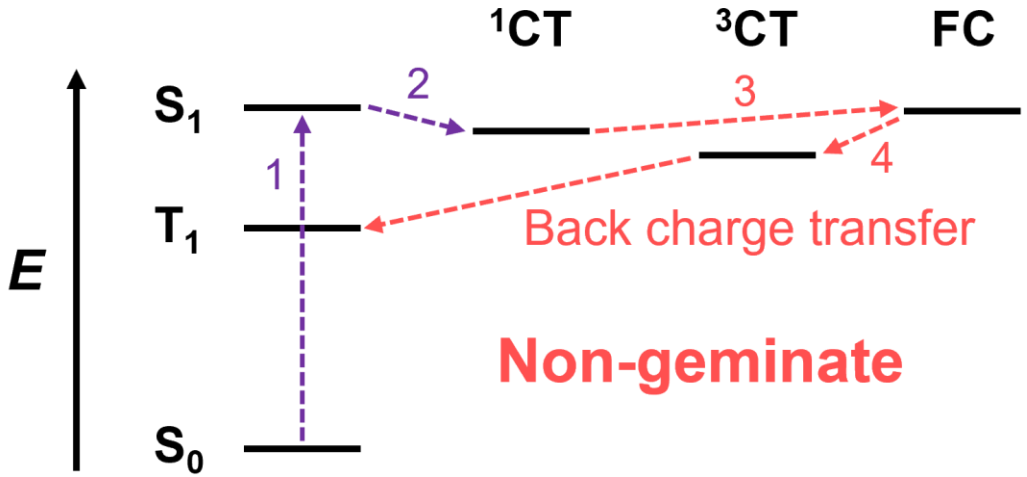




A. J. Gillett *et al.*, *Nature*, 2021, **597**, 666 – 671

Identifying the triplet formation mechanism





- Non-geminate triplet formation is the dominant triplet mechanism in (good) OPVs

A. J. Gillett *et al.*, *Nature*, 2021, **597**, 666 – 671

Impact of triplets on device performance

$\alpha \sim 0.9$ in PM6:Y6

$$\frac{dN_T}{dt} = -\alpha \frac{dN_C}{dt} - \beta N_T N_C$$

Kinetic model fitted to the TA to extract triplet recombination fraction, α

A. J. Gillett *et al.*, *Nature*, 2021, **597**, 666 – 671

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$$\frac{dN_T}{dt} = -\alpha \frac{dN_C}{dt} - \beta N_T N_C$$

$$\chi = 1 - \alpha$$

Fraction of recombination events that can result in photon emission i.e. spin-singlet states

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$\chi \sim 0.1$

$$EQE_{EL} = \gamma \Phi_{PL} \chi \eta_{out}$$

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EQE_{EL} reduced by a factor of 10

$$\Delta V_{nr} = \frac{k_B T}{q} \ln\left(\frac{1}{EQE_{EL}}\right)$$

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Open circuit voltage of solar cell reduced by ~60 mV

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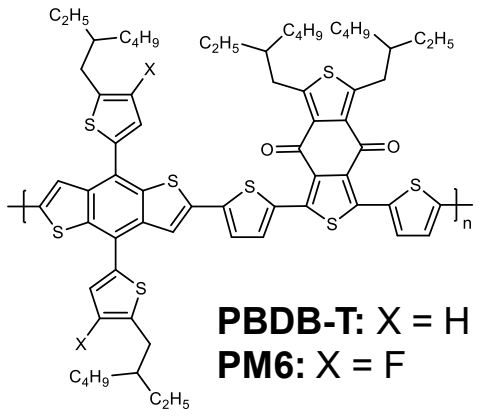
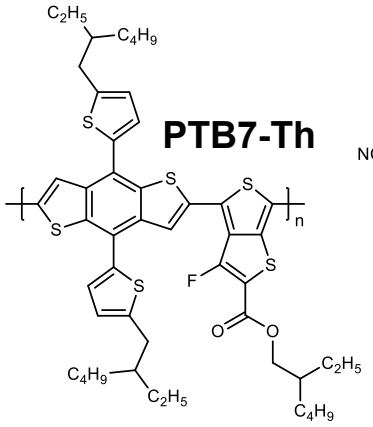
Quyen Nguyen, UCSB
Feng Gao, Linköping U.

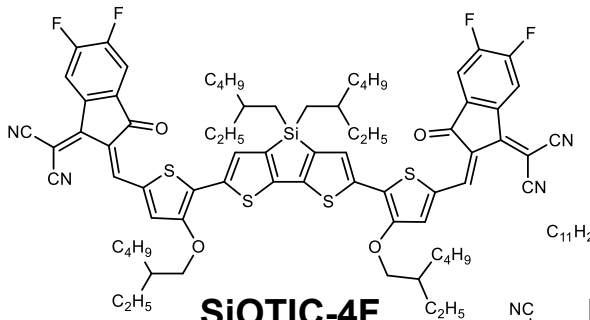
Do all systems produce triplets?



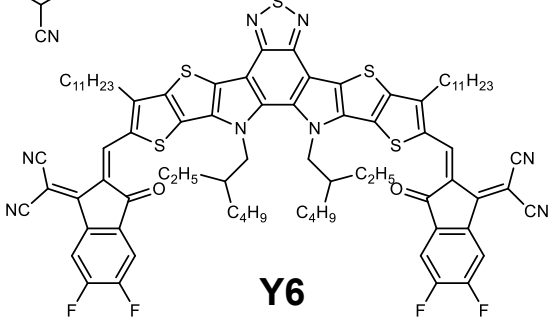
PBDB-T: X = H
PM6: X = F



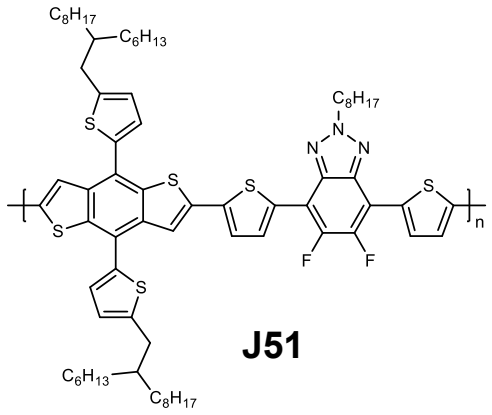
PTB7-Th



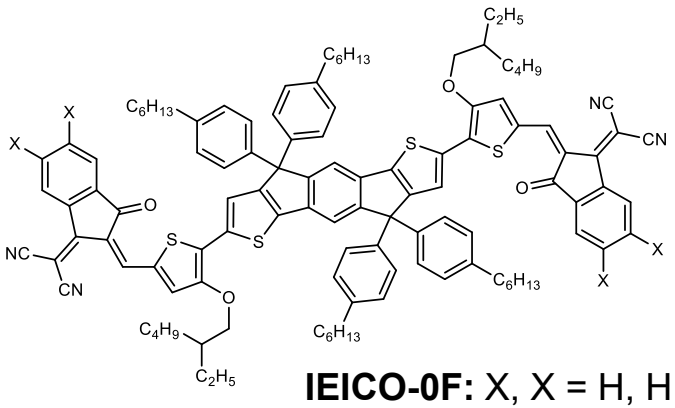
SiOTIC-4F



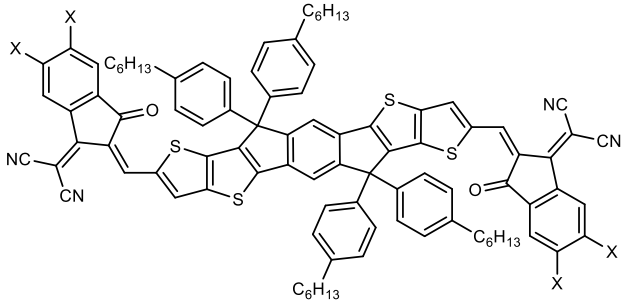
Y6



J51



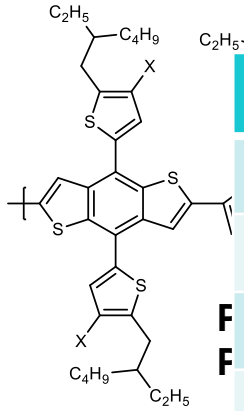
IEICO-0F: X, X = H, H
IEICO-2F: X, X = H, F
IEICO-4F: X, X = F, F

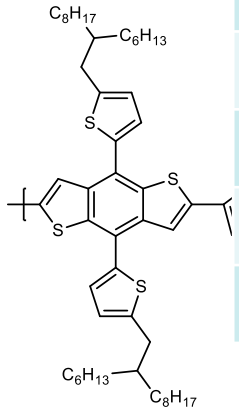


ITIC: X = H
IT-4F: X = F

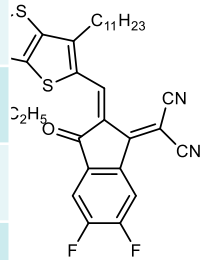
Not all systems produce triplets!

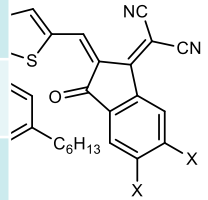
Quyen Nguyen, UCSB
Feng Gao, Linköping U.





Blend	T_1 recombination?
PM6:Y6	Yes
PM6:IT-4F	Yes
PM6:ITIC	Yes
PBDB-T:ITIC	Yes
J51:ITIC	Yes
PTB7-Th: SiOTIC-4F	Yes
PTB7-Th: IEICO-4F	Yes
PTB7-Th: IEICO-2F	No
PTB7-Th: IEICO-0F	No



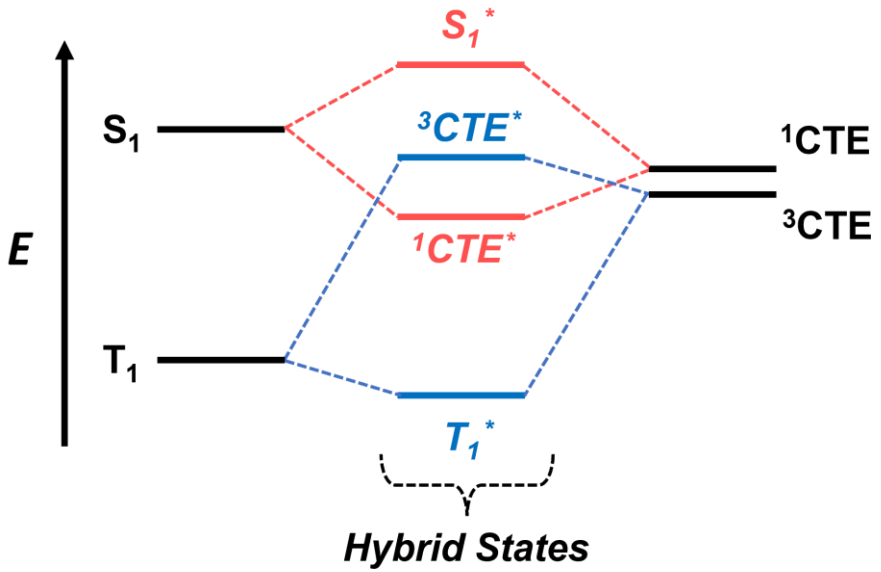


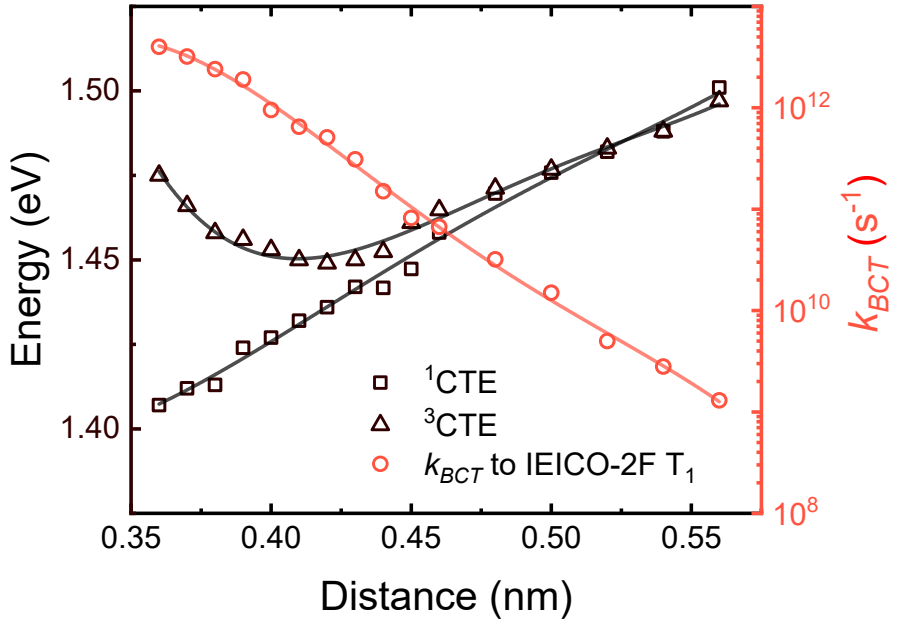
IEICO-2F: X, X = H, F
IEICO-4F: X, X = F, F

ITIC: X = H
IT-4F: X = F

David Beljonne,
U. Mons

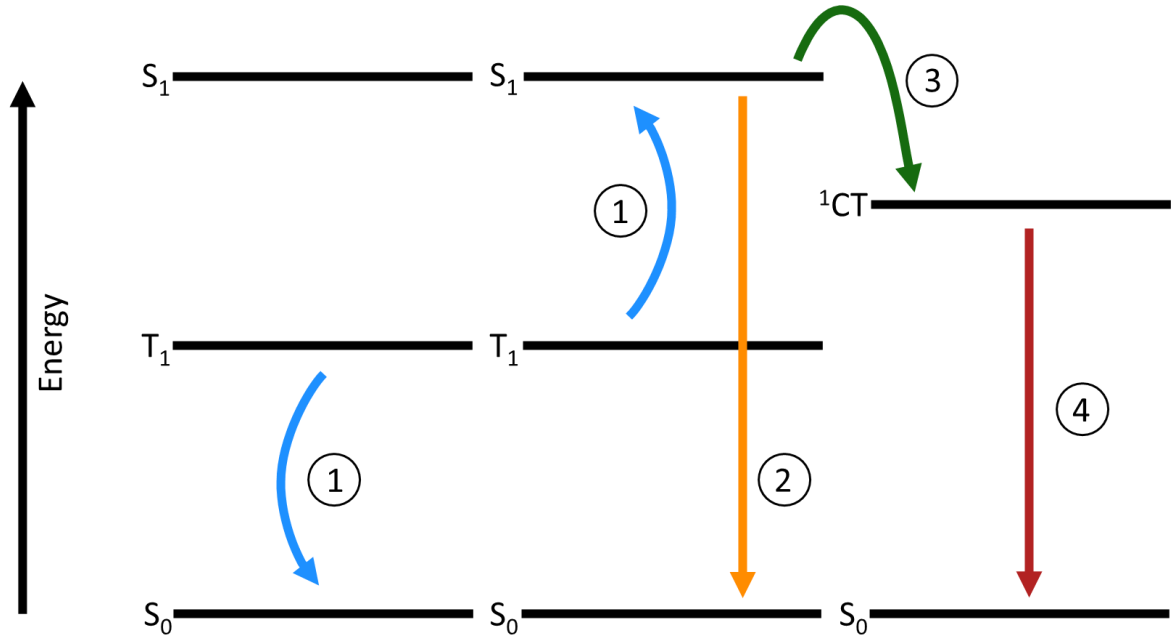
Turning off triplet exciton formation





- Hybridisation between triplet charge transfer and local exciton states
- Inverts the singlet and triplet CT states and blocks triplet exciton formation

Triplet-triplet annihilation in OPVs



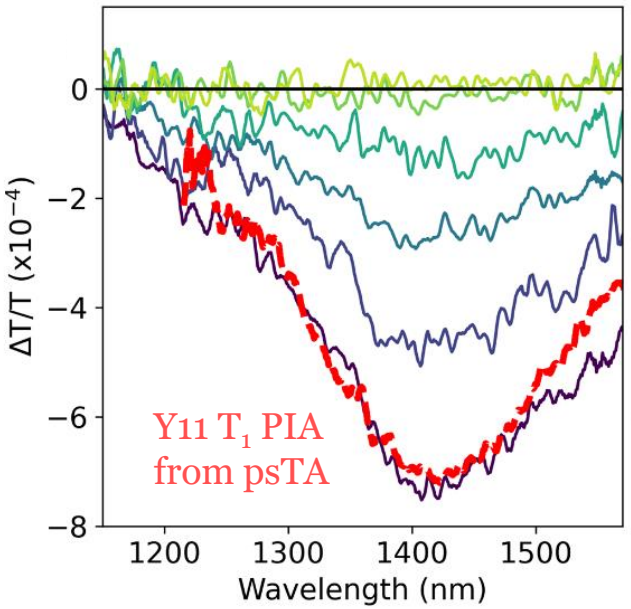
$$EQE_{EL} = \gamma \Phi_{PL} \chi \eta_{out}$$

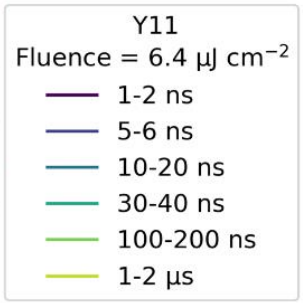
χ increases from 0.25 to 0.625

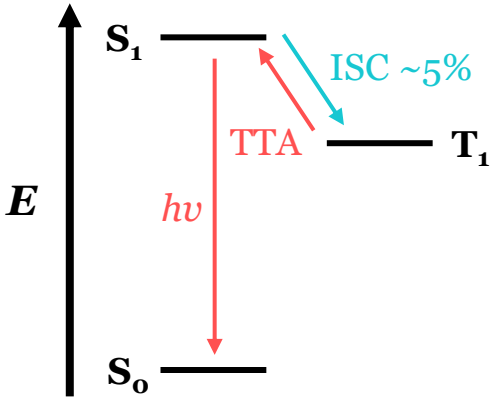
- TTA can recycle (up to) 50% of triplet excitons that would otherwise be lost
- Can mitigate recombination to triplet excitons

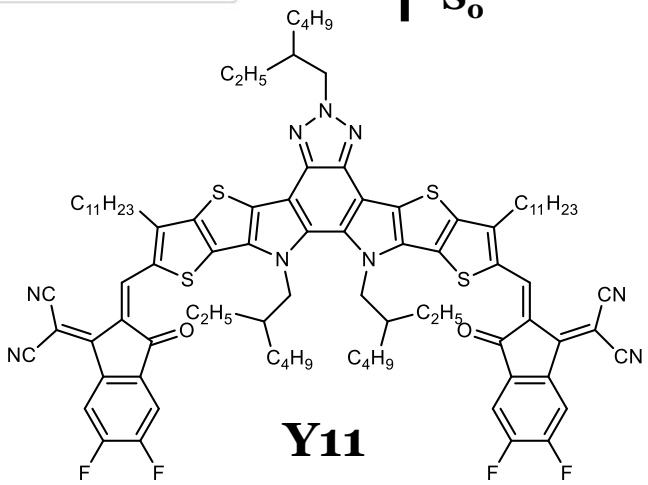
L. J. F. Hart … A. J. Gillett, *Adv. Energy Mater.*, **13(36)**, 2301357

TTA in neat Y11 films





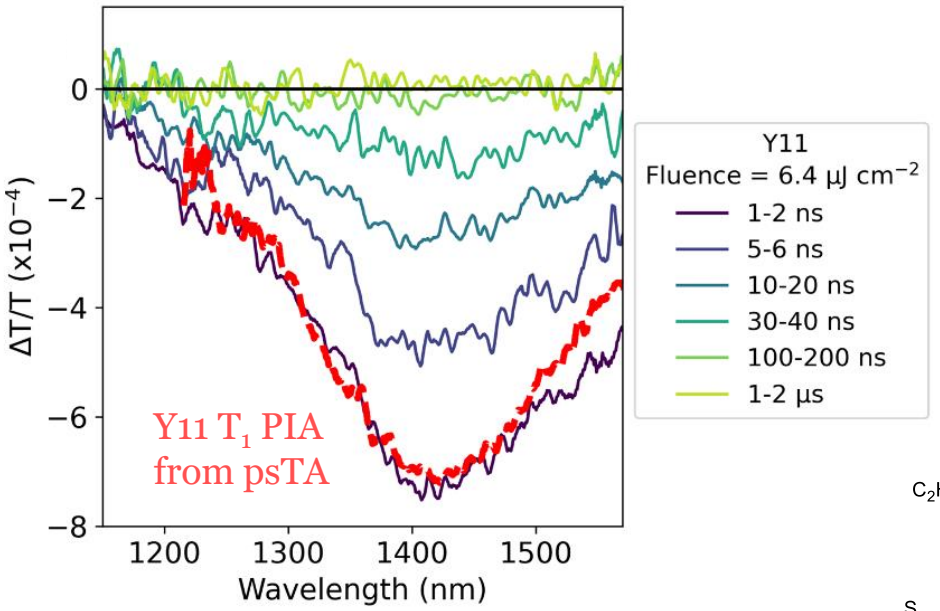


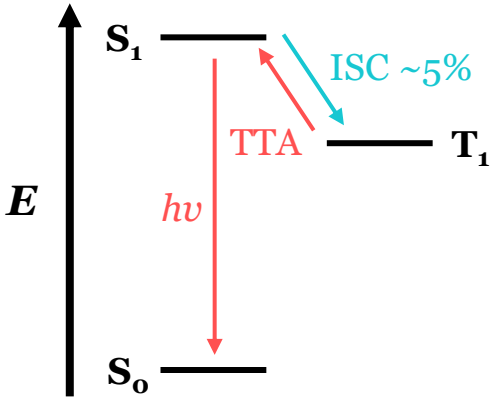


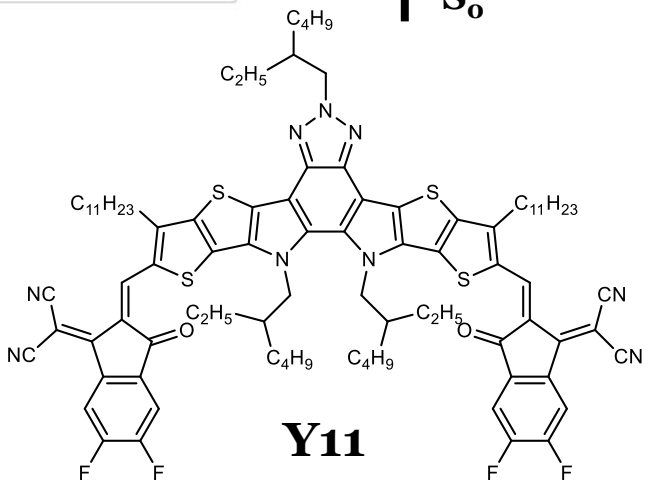
Y11

L. J. F. Hart … A. J. Gillett, A*dv. Energy Mater.*, **13(36)**, 2301357

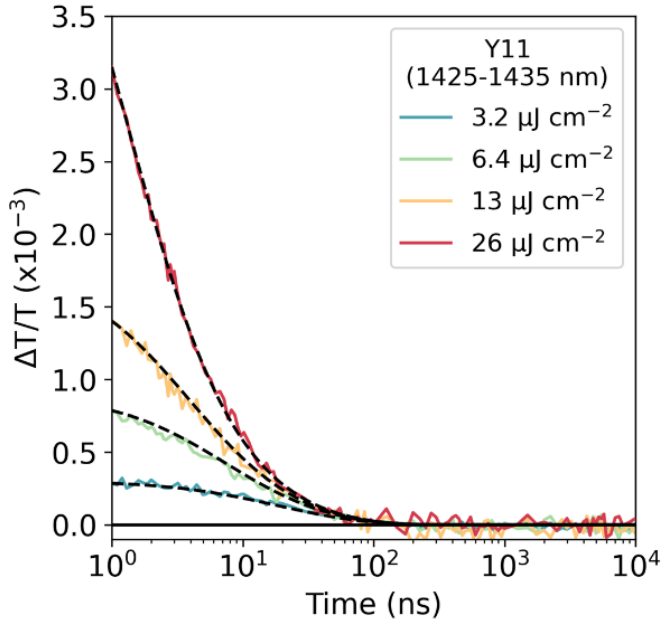
TTA in neat Y11 films







Y11



$$\frac{dn_T}{dt} = -kn_T - \gamma n_T^2$$

Monomolecular triplet decay

TTA

τ = 57 ± 5 ns

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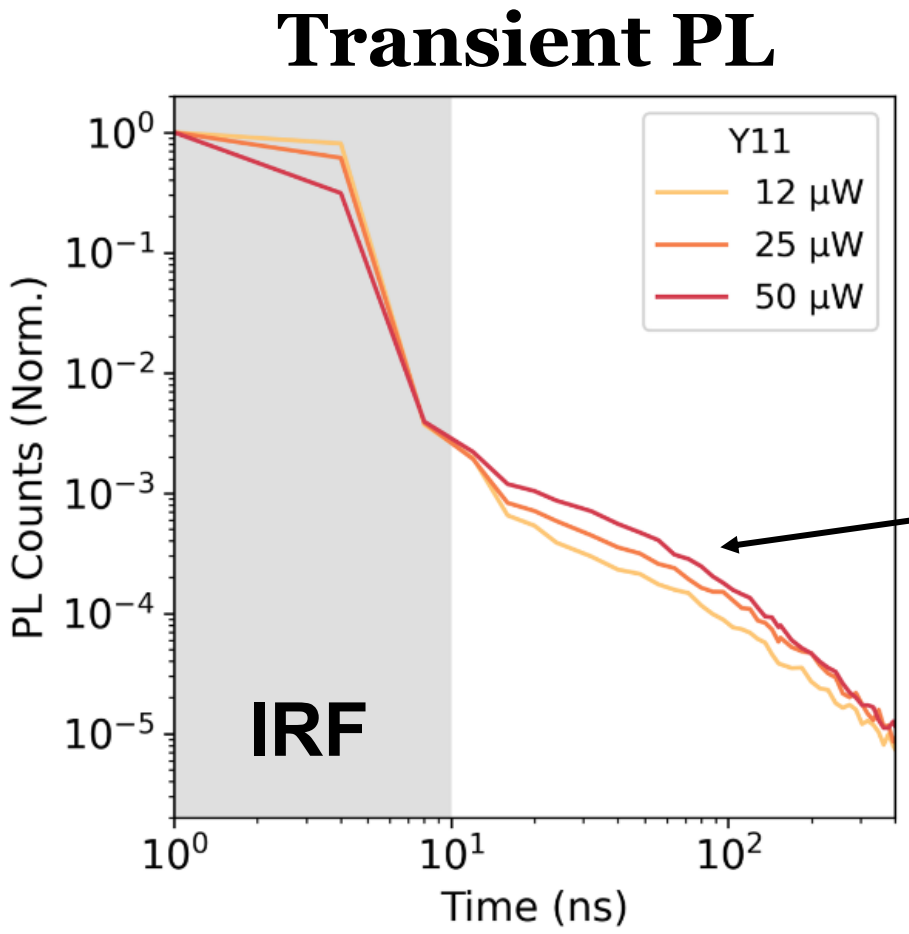
Delayed fluorescence from TTA in Y11



- Pump = 700 nm
- Kinetic from 870 – 900 nm

Fluence-dependent delayed fluorescence

Higher fluence
= higher triplet density
= more intense DF

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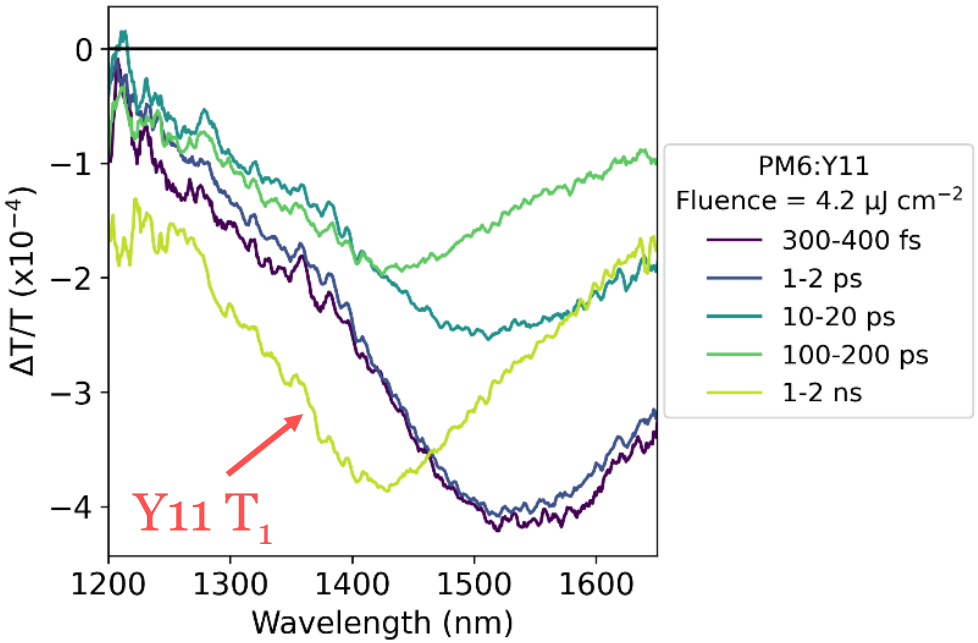
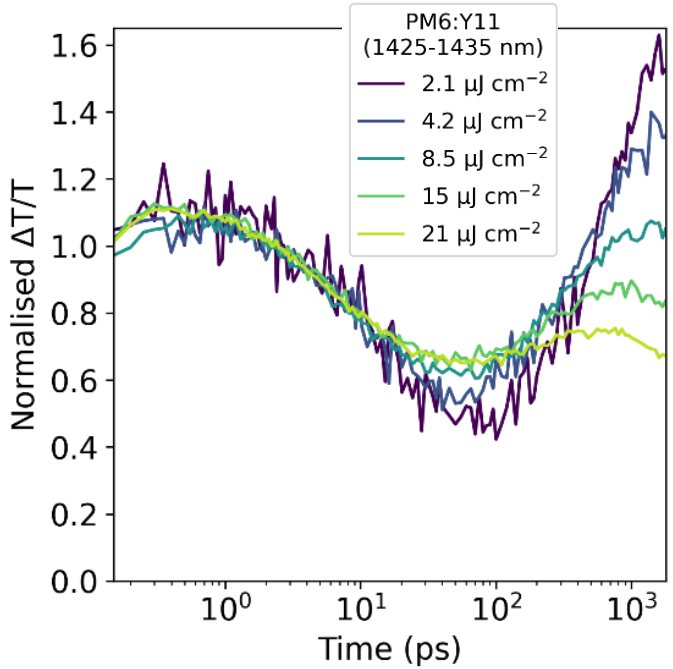
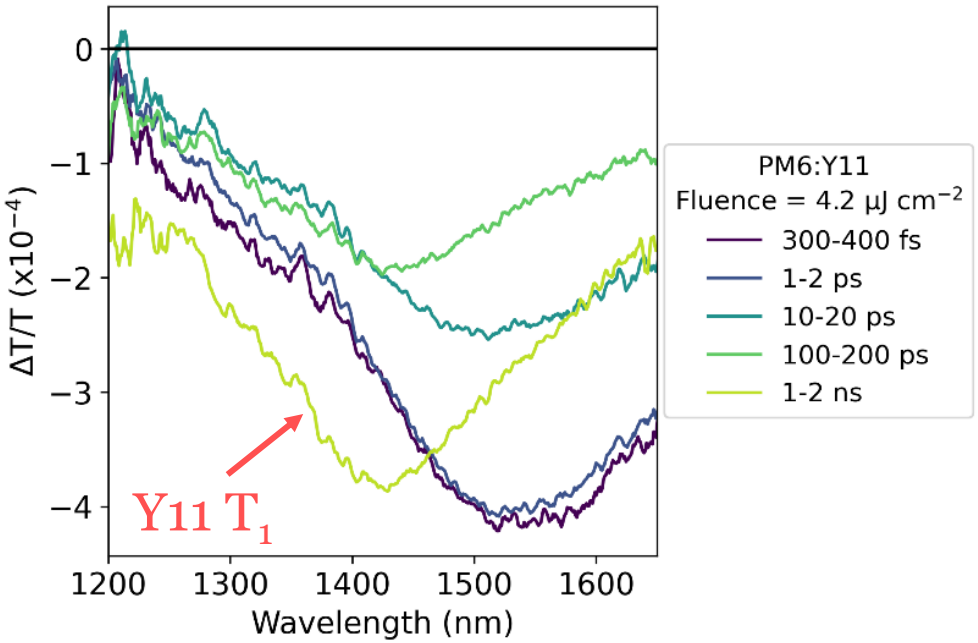
Y11 is a better TTA material than rubrene!

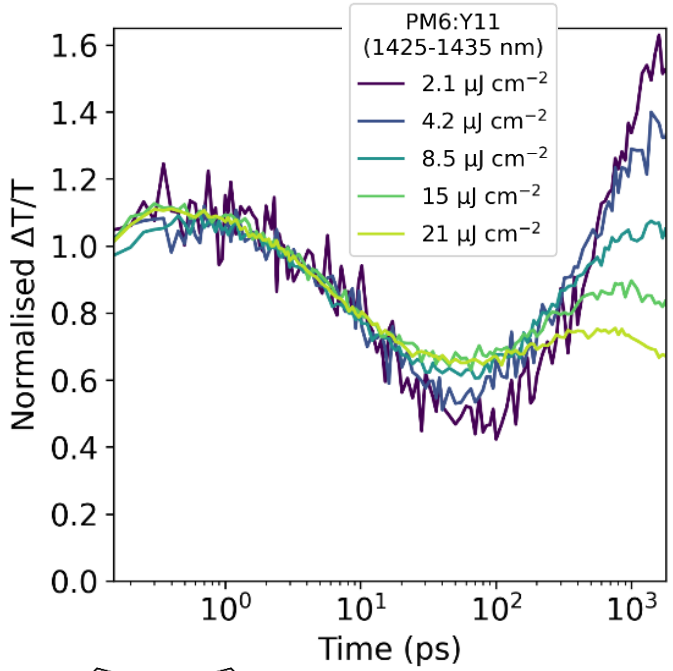




L. J. F. Hart … A. J. Gillett, *Adv. Energy Mater.*, **13(36)**, 2301357

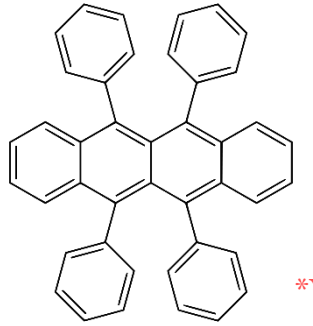
Y11 is a better TTA material than rubrene!





Extracted TTA rate constant in PM6:Y11: ~2.2×10^{-10} cm^3 s^{-1}

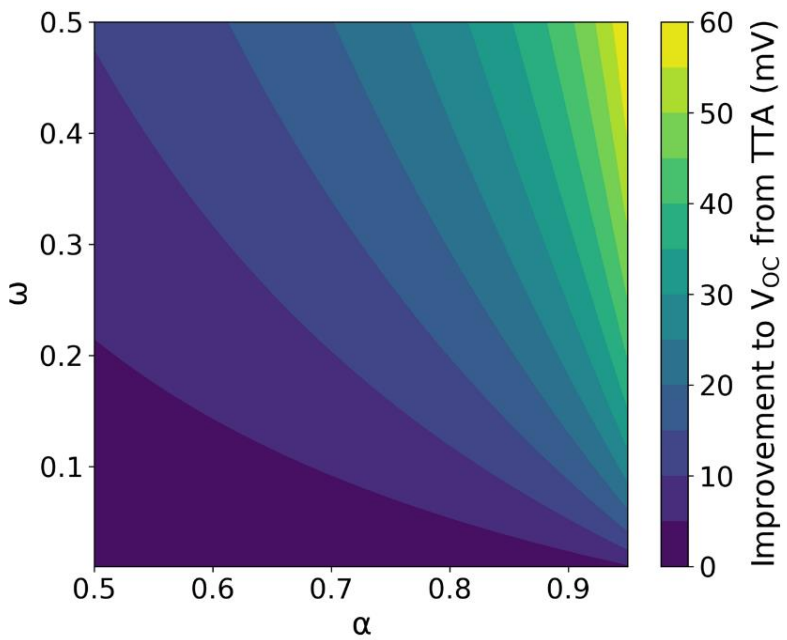
TTA rate constant for rubrene*: ~10^{-13} cm^3 s^{-1}



*Y. Sakamoto et al. *Commun. Mater*, 3, 76 (2022)

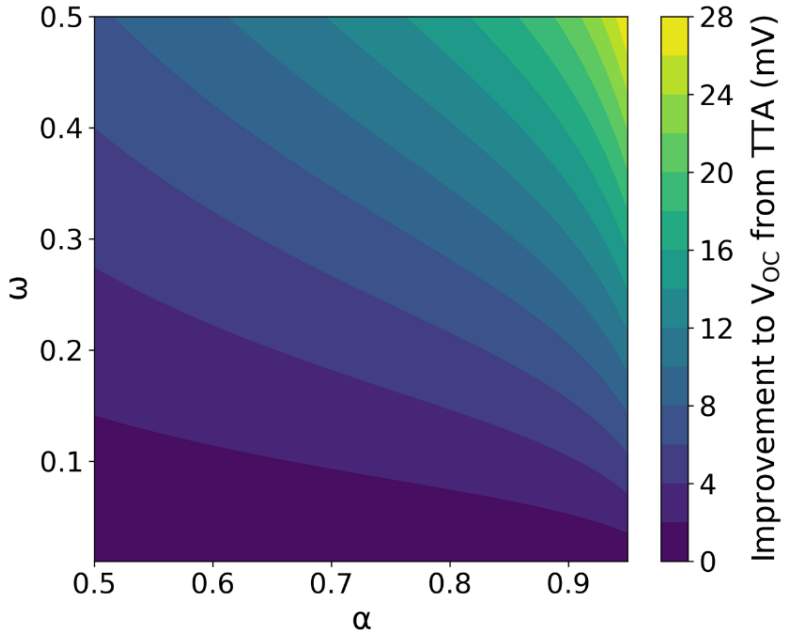
L. J. F. Hart … A. J. Gillett, A*dv. Energy Mater.*, **13(36)**, 2301357

Potential V_{oc} benefits of TTA



If all NFA singlets formed via TTA can emit:

$$\chi = (1-\alpha) + \alpha\omega$$



If all NFA singlets indefinitely recycle into charges:

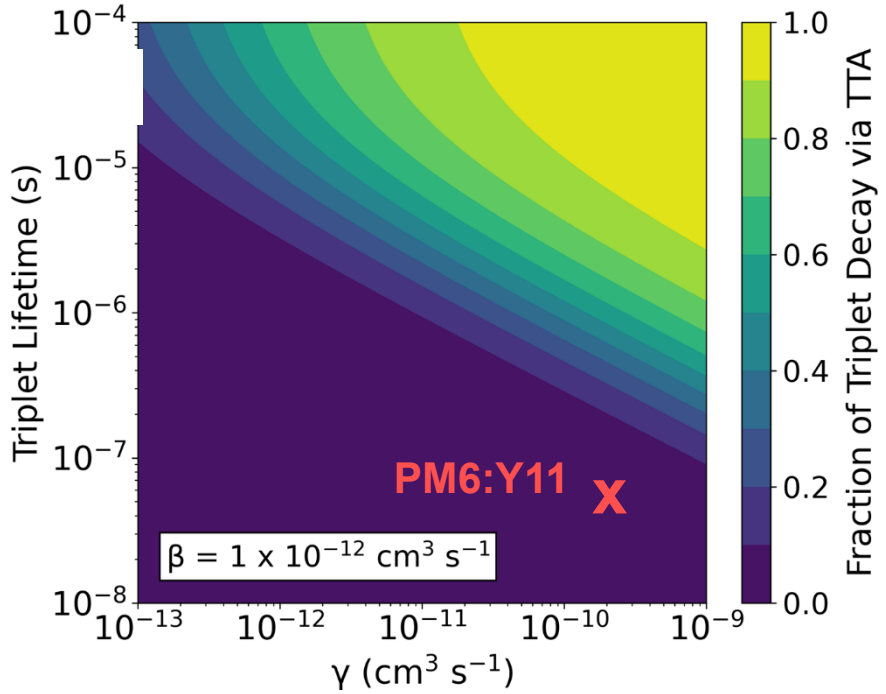
$$\chi = \frac{1 - \alpha + \alpha\omega(1-\eta_{CT})}{1 - \alpha\omega\eta_{CT}}$$

χ = fraction of recombination events with potential for photon emission

$$\boldsymbol{EQE_{EL} = \gamma \Phi_{PL} \chi \eta_{out}}$$

L. J. F. Hart … A. J. Gillett, A*dv. Energy Mater.*, **13(36)**, 2301357

What is the situation in PM6:Y11?



Parameters used*:

*J. Wu, et al. *Energy Environ. Sci.* **13**, 2422-2430 (2020)

$\alpha = 0.75$

$n_P = 4.5 \times 10^{16}$ cm^{-3}

$k_2 = 1 \times 10^{-11}$ cm^3 s^{-1}

TTA rate constant = 2.2×10^{-10} cm^3 s^{-1}

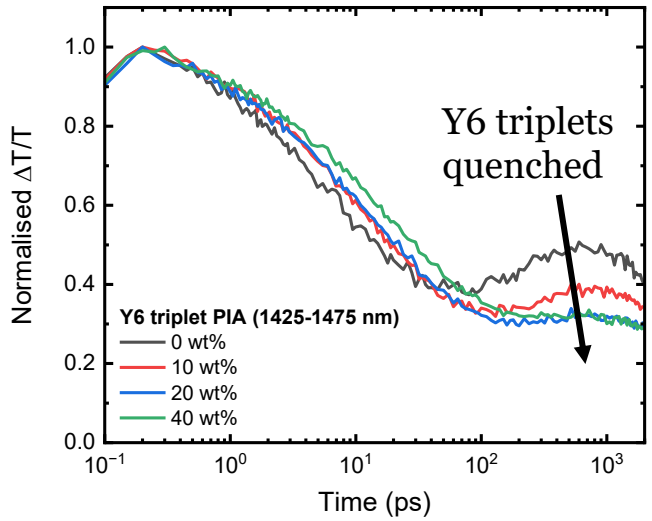
Monomolecular T_1 lifetime = 57 ± 5 ns

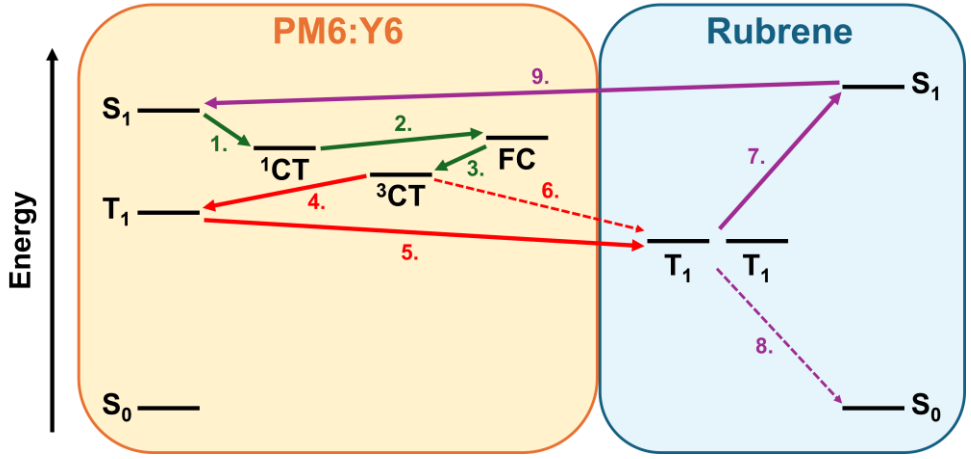
- Y11 monomolecular triplet lifetime too short for significant TTA at 1-Sun carrier densities
- A triplet lifetime on the order of ~1 μs is necessary for TTA to improve V_{OC}

L. J. F. Hart … A. J. Gillett, A*dv. Energy Mater.*, **13(36)**, 2301357

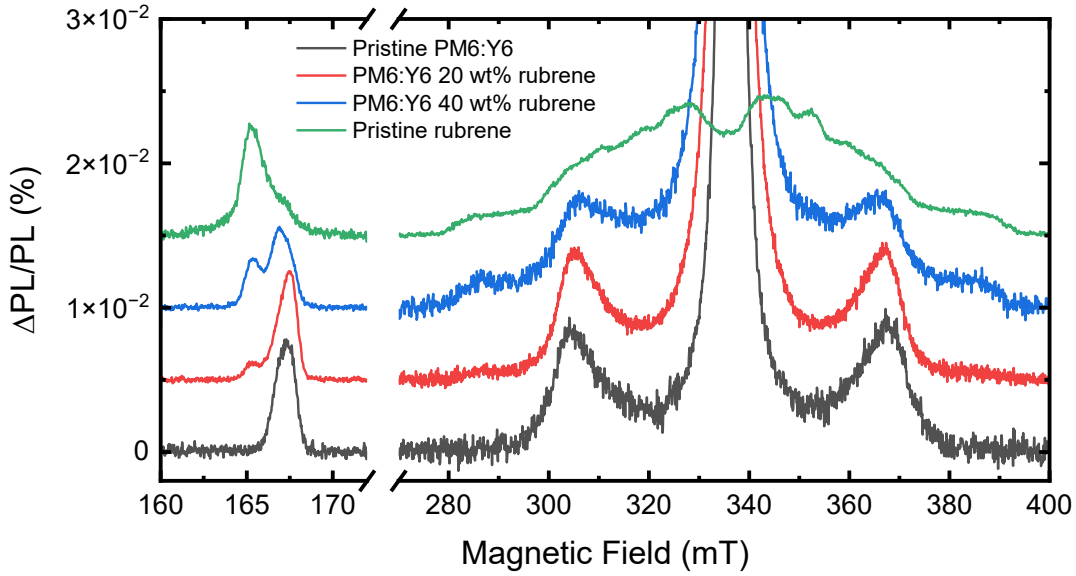
Rubrene as a TTA mediator in PM6:Y6

Darcy Unson, Cambridge



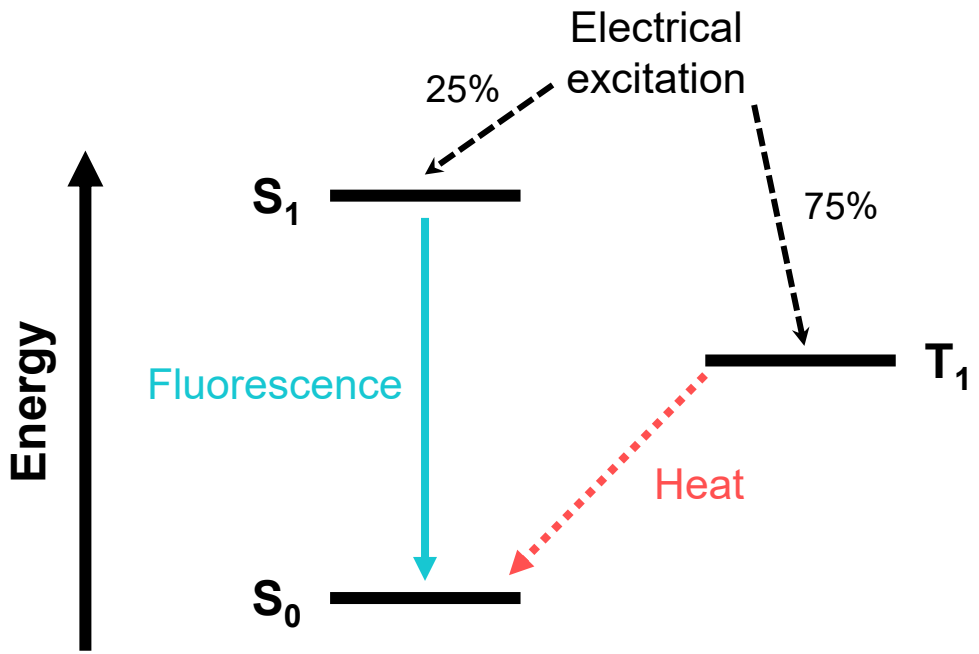


Photoluminescence-detected magnetic resonance (PLDMR)



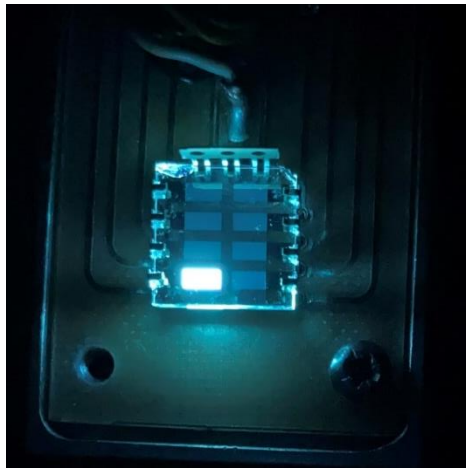
Pump = 785 nm
Detection >830 nm

Spin state engineering in OLEDs



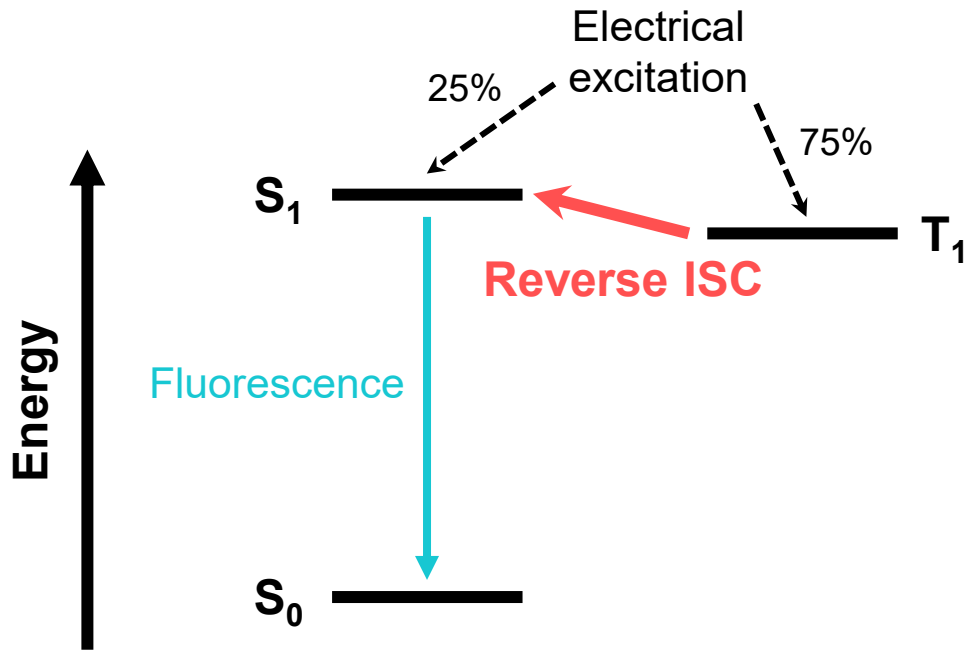
IQE limited to 25%!

- Spin is a critical consideration for OLED operation
- Spin-triplet excitons generally decay without photon emission



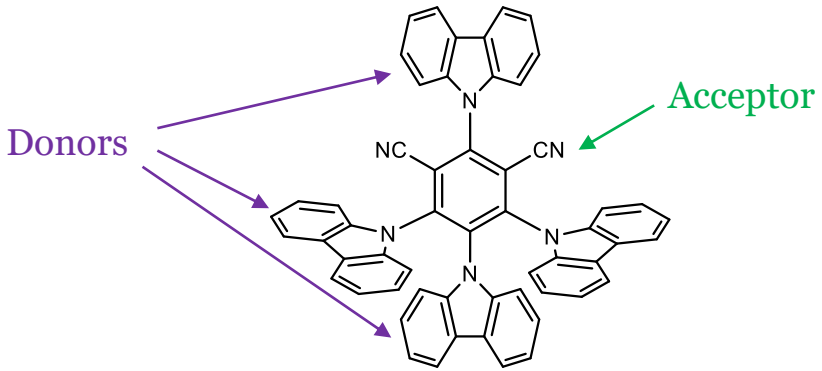
OLED test device, made in Cambridge

Thermally-activated delayed fluorescence



IQE ~100%!

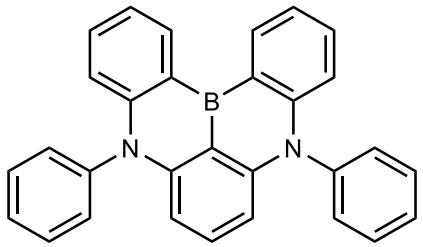
- TADF materials have a small (<100 meV) singlet-triplet energy gap
- T_1 can be upconverted to S_1 through ambient thermal energy
- Donor-acceptor structure with **long range charge transfer**-type excited states reduces electron exchange energy



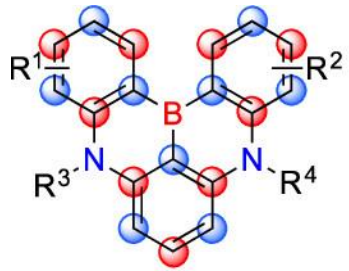
4CzIPN – an archetypal TADF emitter

H. Uoyama *et al.*, *Nature*, 2012, **492**, 234 – 238

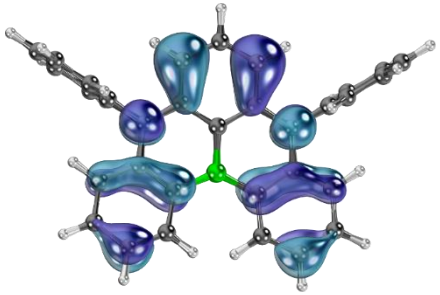
‘Multiple-resonance’ TADFs



DABNA-1

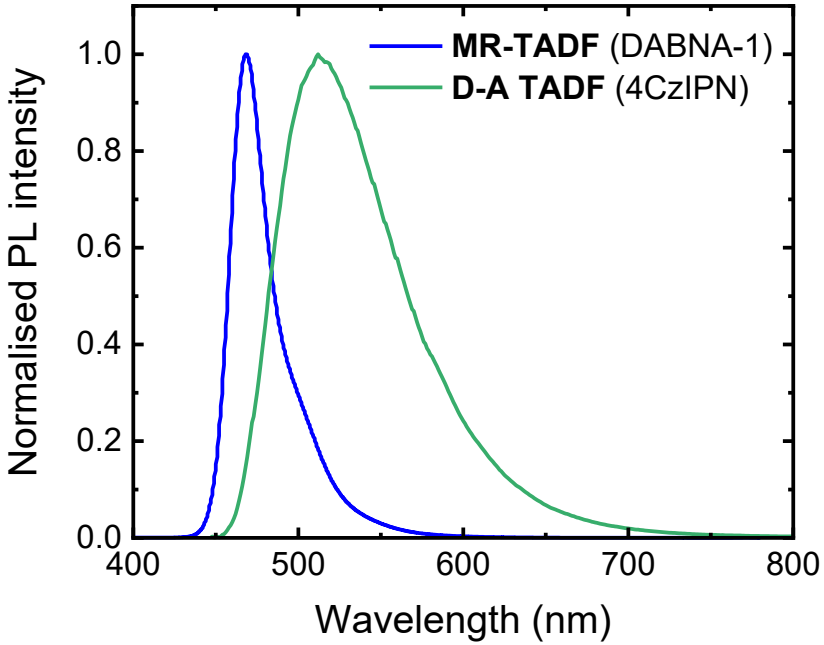


: HOMO
: LUMO



HOMO

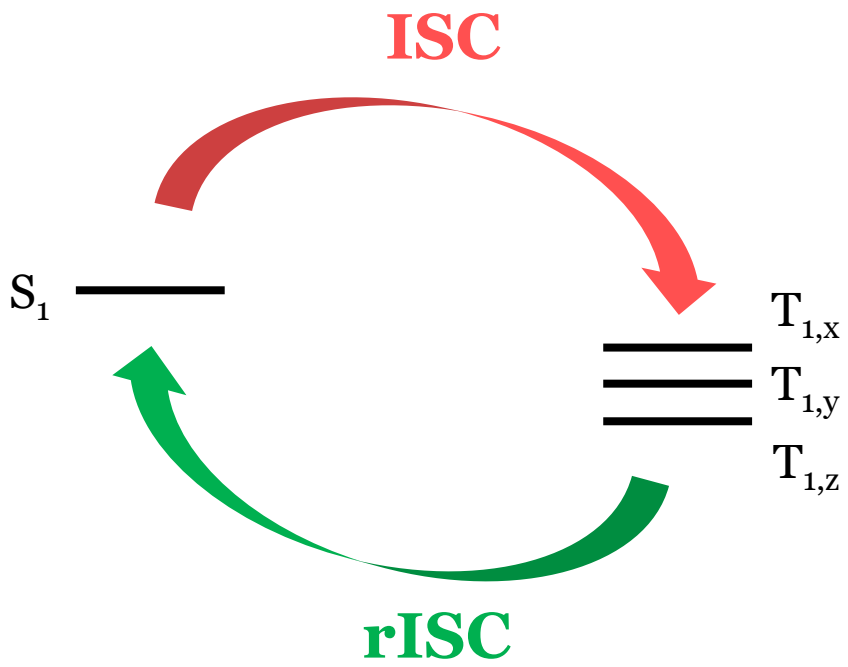
LUMO



- Narrowband blue emission
- **<u>Short range charge transfer</u>** reduces S_1-T_1 energy gap whilst maintaining oscillator strength

T. Hatakeyama *et al.*, *Adv. Mat.*, 2016, **28(14)**, 2777 – 2781

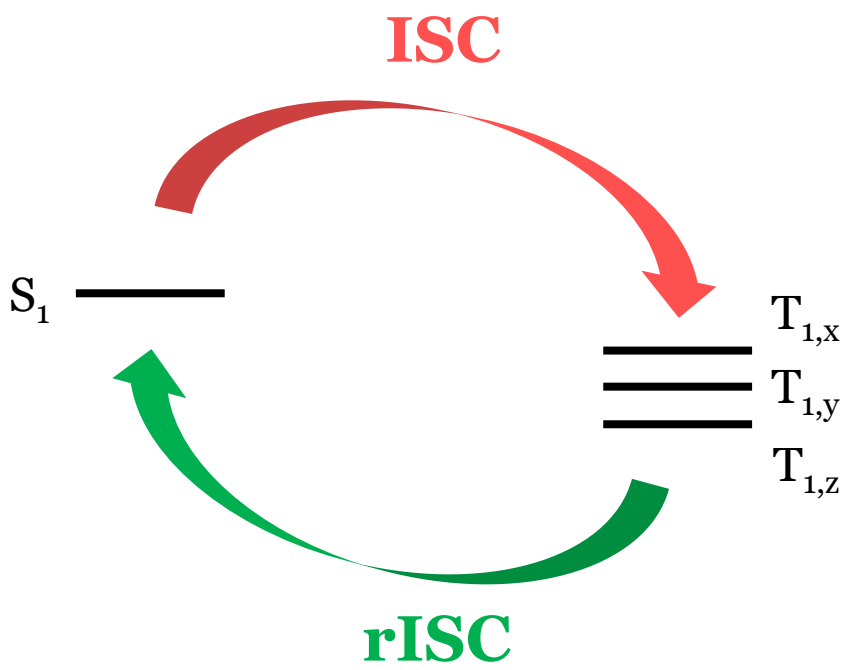
Building a complete picture of (r)ISC



- Which triplet sublevels mediate (r)ISC?
- What role (if any) of vibrations in driving (r)ISC
- Can the mechanism predicted computationally be verified experimentally?

Computational picture of (r)ISC

Danillo Valverde
Gaetano Ricci
Yoann Olivier, U. Namur



$$\langle \psi_{S_1} | H_{SOC} | \psi_{T_{1,\alpha}} \rangle$$

$$\langle SOC^2 \rangle = \langle SOC \rangle^2 + \sigma^2$$

'static' SOC from molecular symmetry

Contribution from symmetry-breaking vibrations

$$p_x \propto |SOC_x|^2$$

$$p_y \propto |SOC_y|^2$$

$$p_z \propto |SOC_z|^2$$

Unpublished work

Computational picture of (r)ISC

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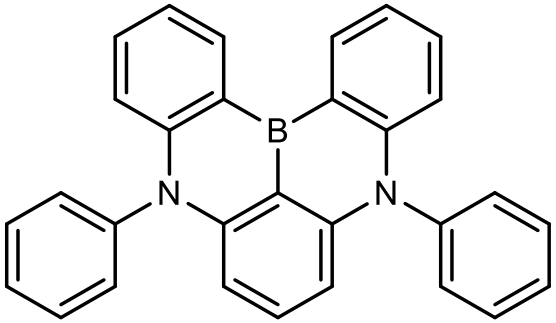
Gaetano Ricci
Yoann Olivier, U. Namur



DABNA-1

$(SOC_x)_{eq}$	σ_x	$(SOC_y)_{eq}$	σ_y	$(SOC_z)_{eq}$	σ_z
0	0	0	0.24	0.03	0.04

$\sqrt{\langle SOC_x^2 \rangle}$	$\sqrt{\langle SOC_y^2 \rangle}$	$\sqrt{\langle SOC_z^2 \rangle}$
0	0.24	0.05

(in cm^{-1})

Computational picture of (r)ISC

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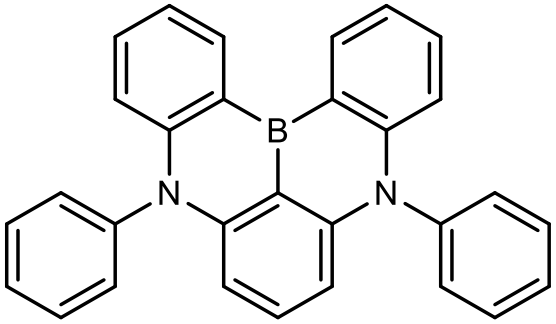
Gaetano Ricci
Yoann Olivier, U. Namur



DABNA-1

$(SOC_x)_{eq}$	σ_x	$(SOC_y)_{eq}$	σ_y	$(SOC_z)_{eq}$	σ_z
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$\sqrt{\langle SOC_x^2 \rangle}$	$\sqrt{\langle SOC_y^2 \rangle}$	$\sqrt{\langle SOC_z^2 \rangle}$
0	0.24	0.05

(in cm^{-1})

$$\sqrt{\langle SOC^2 \rangle} = \quad 0.25\ cm^{-1}$$

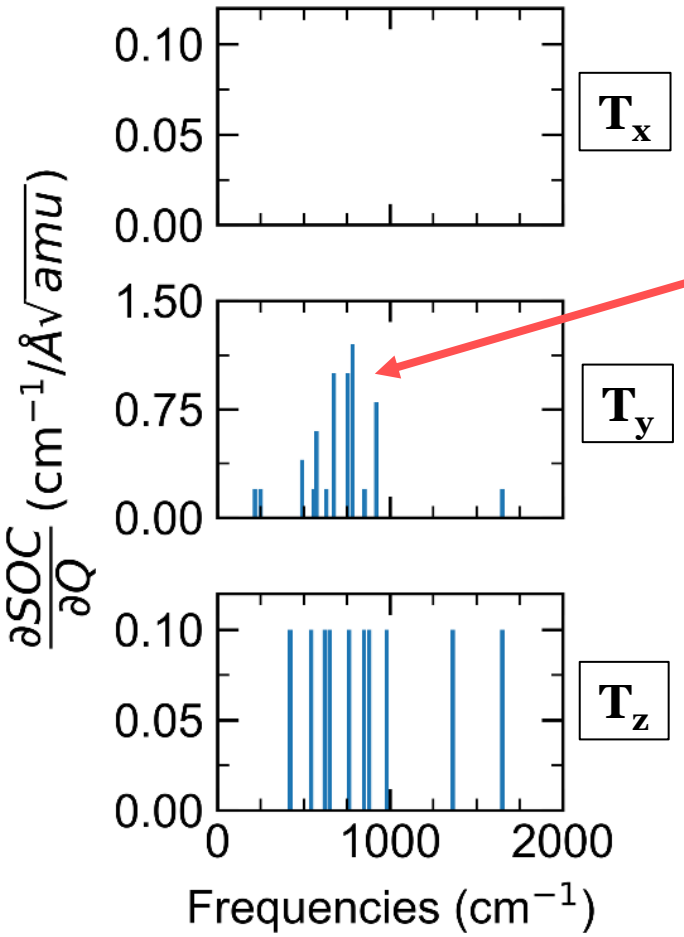
$$\frac{p_y}{p_z} = \frac{\langle SOC_y^2 \rangle}{\langle SOC_z^2 \rangle} = \frac{0.24^2}{0.05^2} = 25 = \frac{p_y}{1 - p_y}$$

$$\boldsymbol{p_x = 0} \quad \boldsymbol{p_y = \frac{25}{26} = 0.96} \quad \boldsymbol{p_z = 0.04}$$

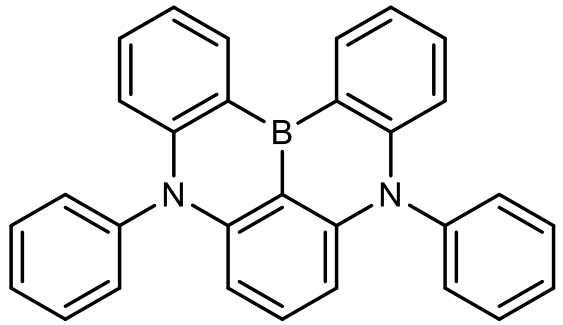
Unpublished work

(r)ISC is driven by vibrations

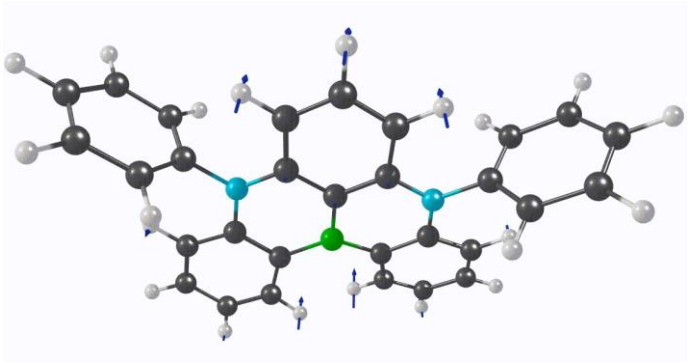
Danillo Valverde
Gaetano Ricci
Yoann Olivier, U. Namur



Cluster of modes around 600-800 cm^{-1} drive ISC



DABNA-1



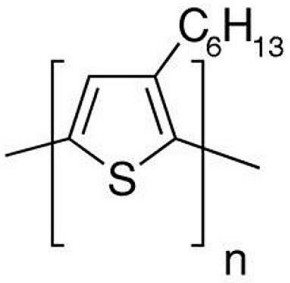
782 cm^{-1}

Unpublished work

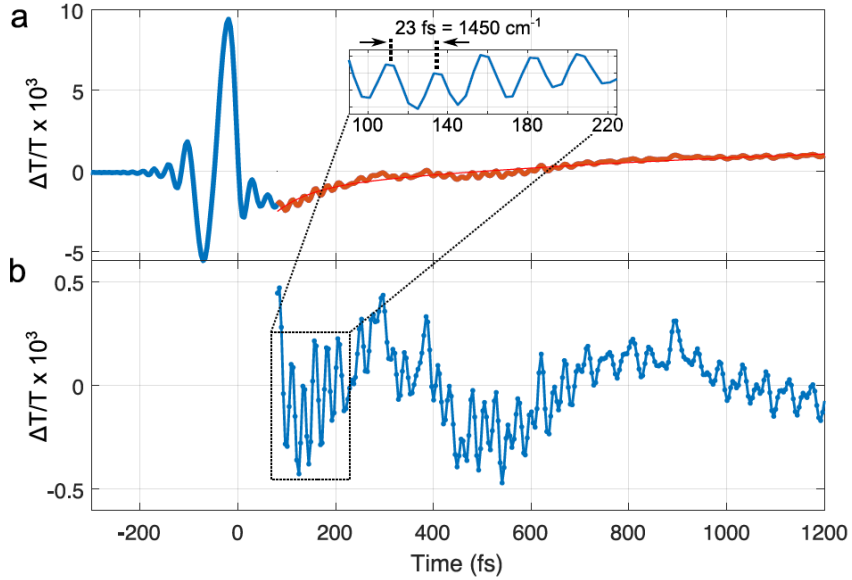
Impulsive Vibrational Spectroscopy - measuring vibrations with light

- TAS measurement with a very short (~10 fs) pump pulse
- 10 fs pulse of light is the ‘hammer’ making the molecular vibrational modes ‘ring’ coherently
- Can observe the excited state vibrational couplings in the TAS measurement

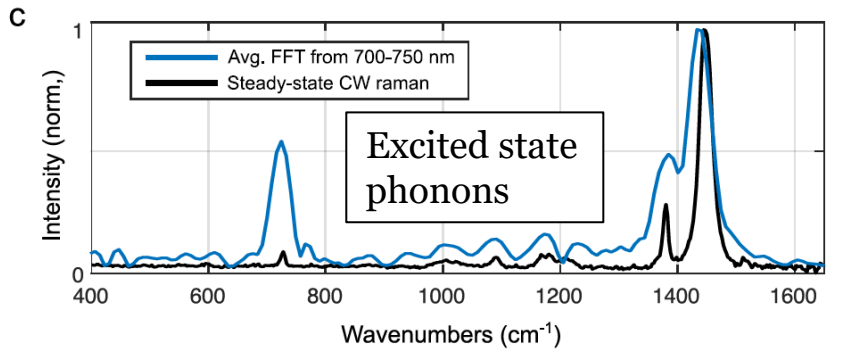
Impulsive Vibrational Spectroscopy - measuring vibrations with light



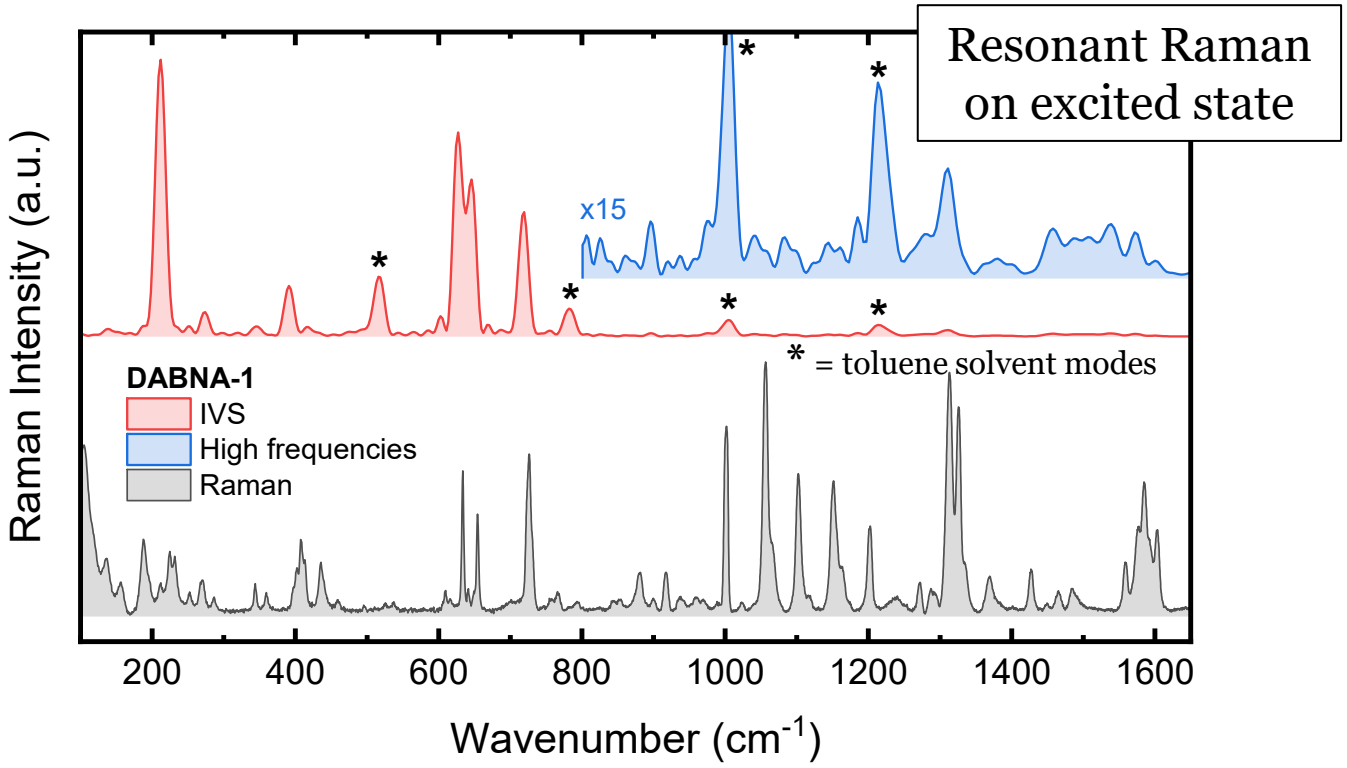
Data from p3HT



- TAS measurement with a very short (~10 fs) pump pulse
- 10 fs pulse of light is the 'hammer' making the molecular vibrational modes 'ring' coherently
- Can observe the excited state vibrational couplings in the TAS measurement

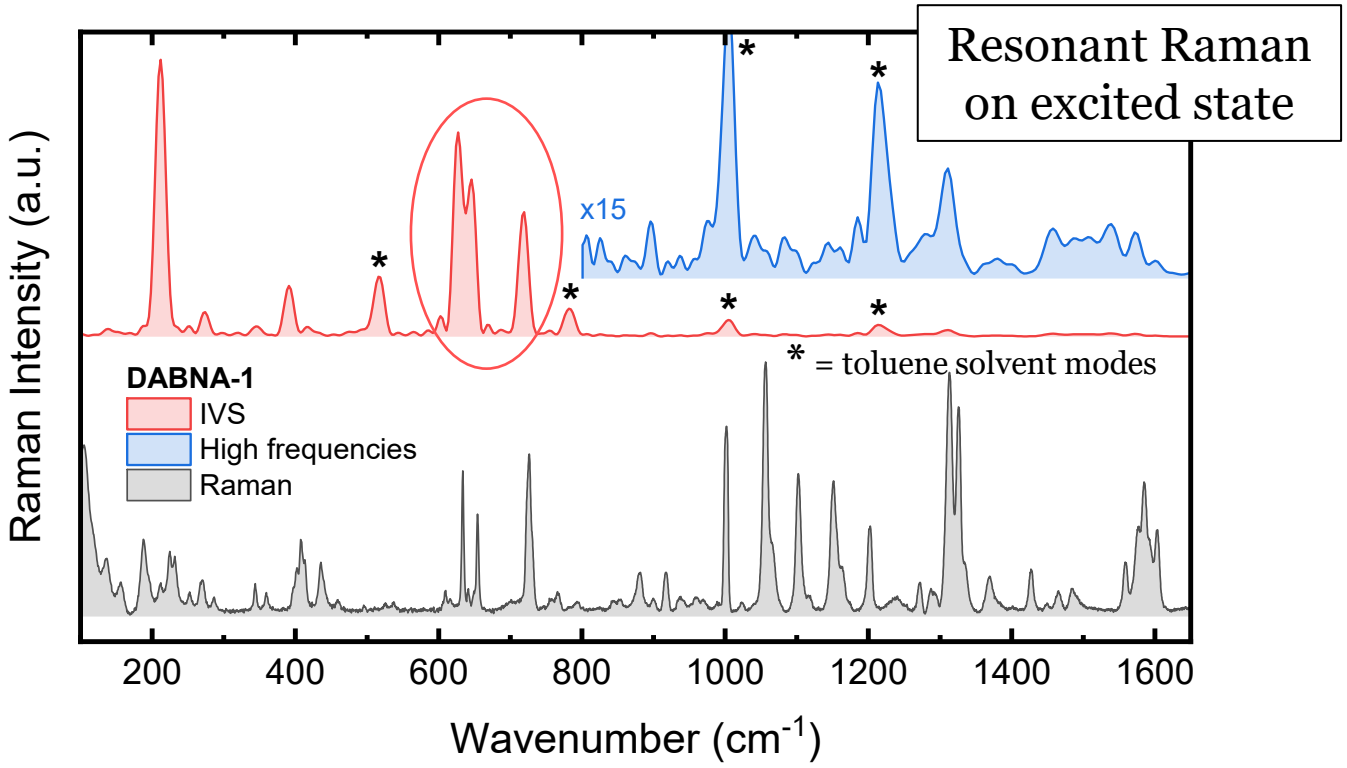


IVS of DABNA-1

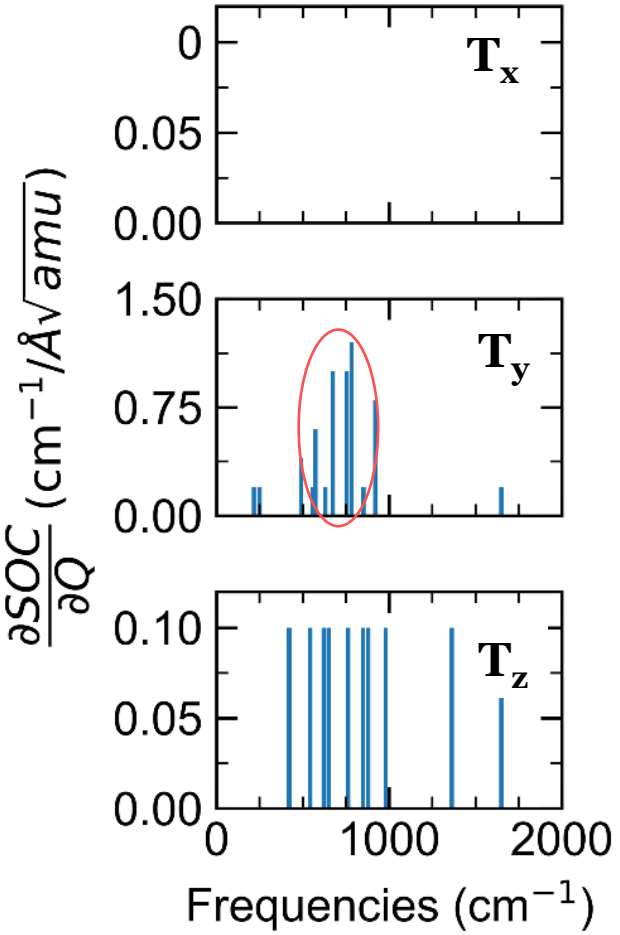


Unpublished work

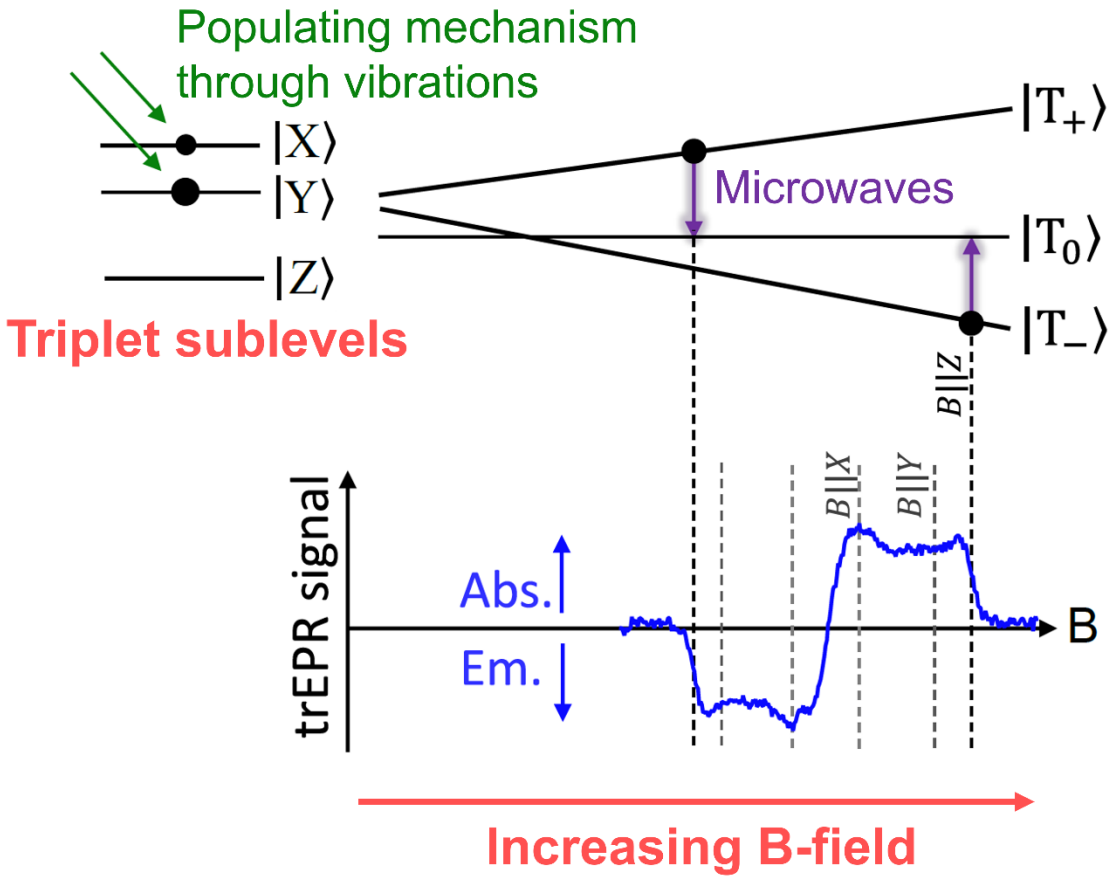
IVS of DABNA-1



IVS confirms that modes around 600-800 cm^{-1} are strongly coupled to the S_1 excited state



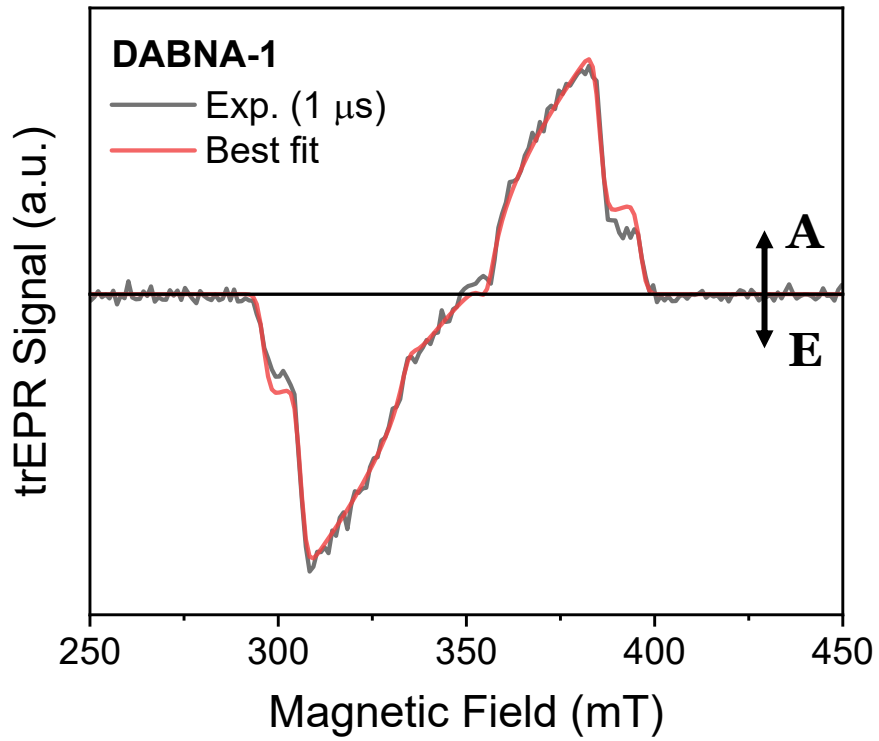
Transient EPR provides sublevel populations



Schematic by Jeannine Grüne

trEPR confirms ISC mechanism

Jeannine Grüne, Cambridge
Alberto Privitera, U. Florence



Predicted by theory

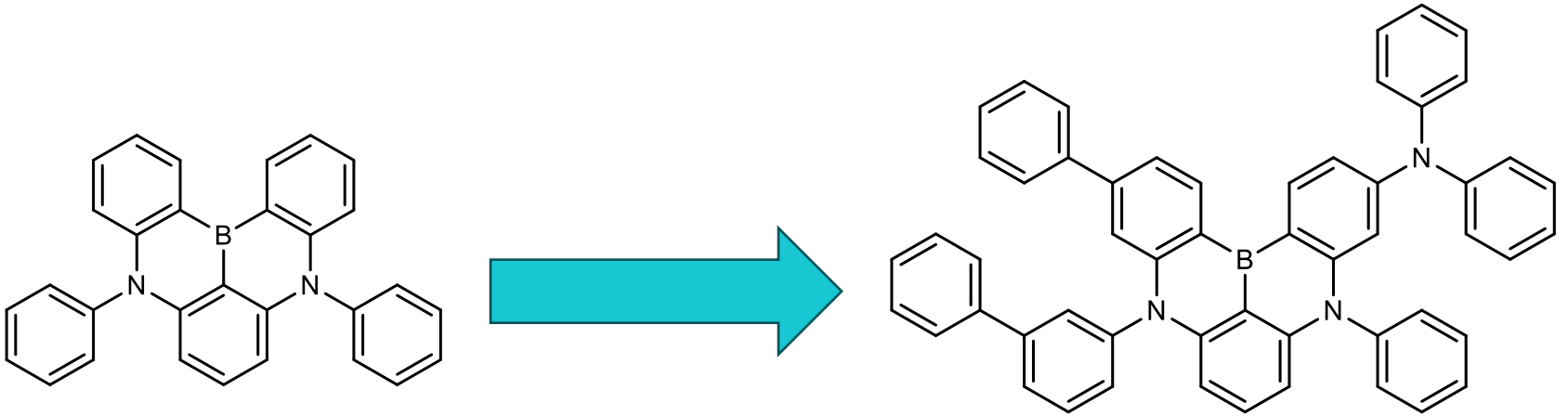
$p_x = 0$ $p_y = 0.96$ $p_z = 0.04$

trEPR simulation

$p_x = 0$ $p_y = 0.77$ $p_z = 0.23$

Unpublished work

What about other DABNA-based emitters?

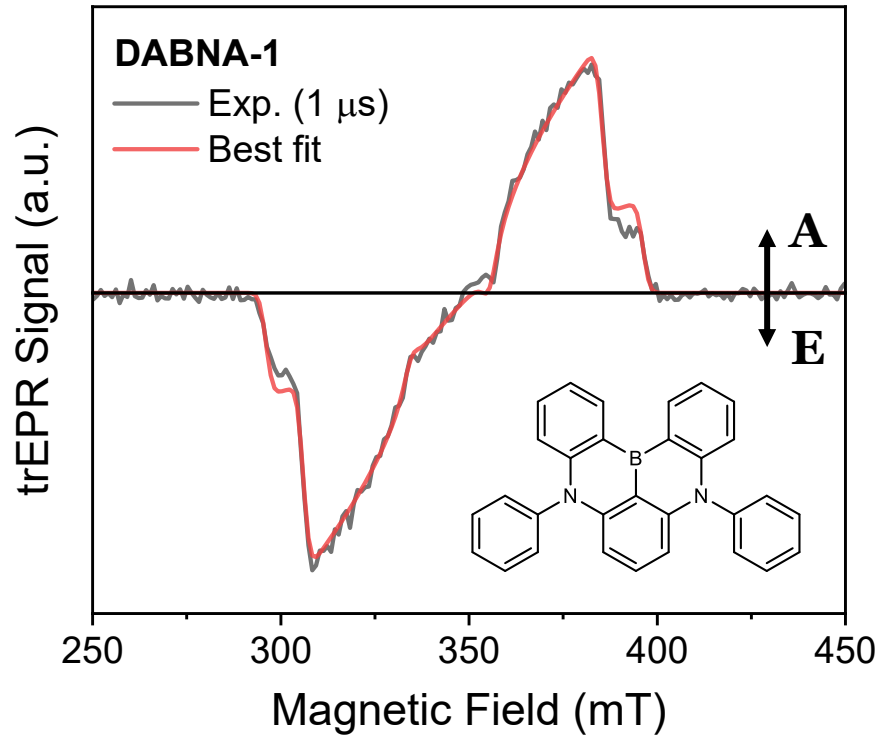


DABNA-1 **DABNA-2**

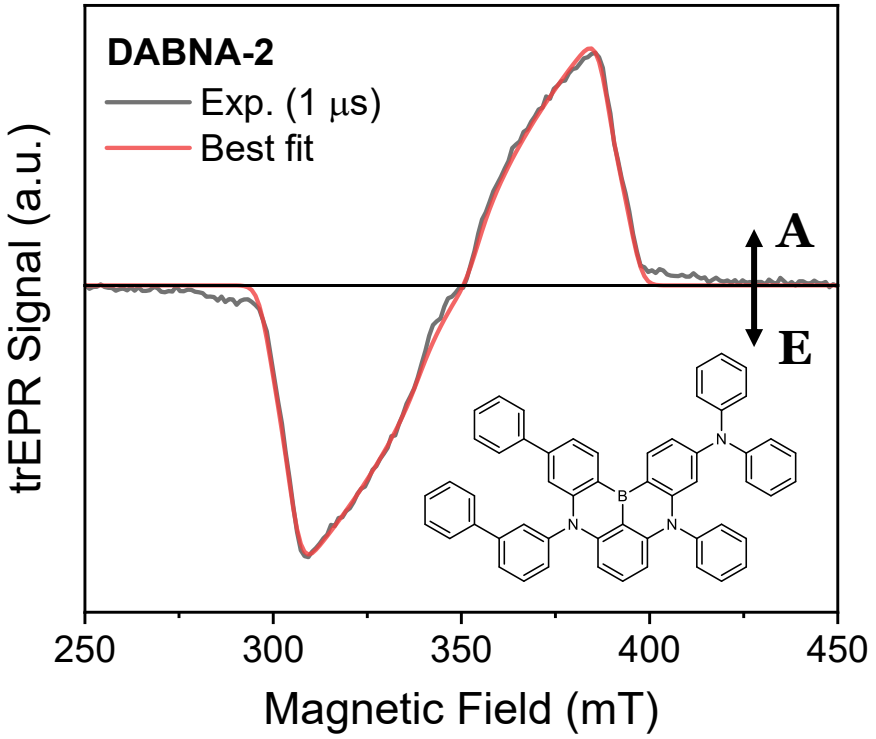
- DABNA-1 is a poor TADF emitter due to low SOC and relatively large ΔE_{ST}
- Many MR-TADFs are composed of the DABNA-1 core with additional peripheral groups attached which improve the rISC rate
- What impact do these groups have on the ISC mechanism of DABNA-2?

Unpublished work

ISC mechanism controlled by the core



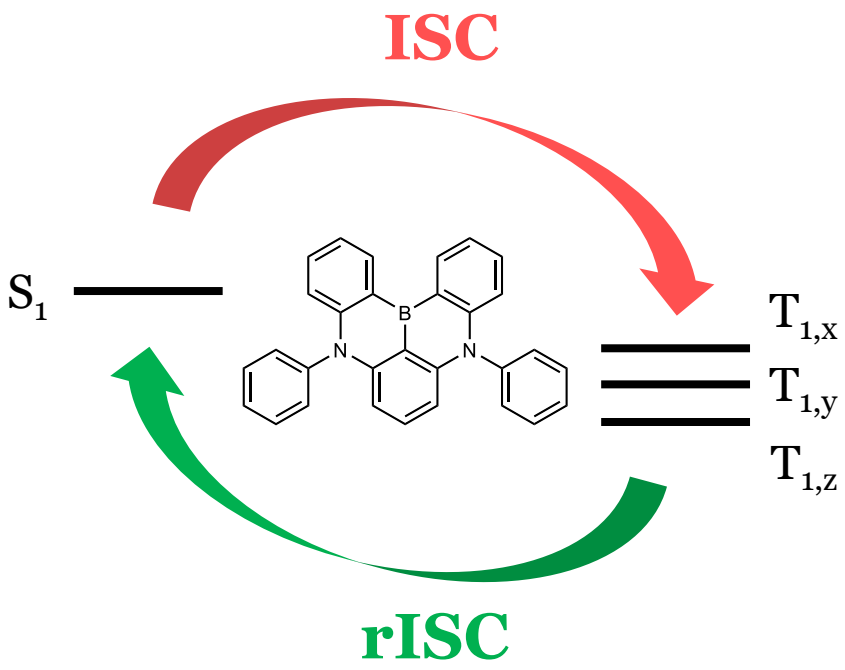
$p_x = 0$ $p_y = 0.77$ $p_z = 0.23$

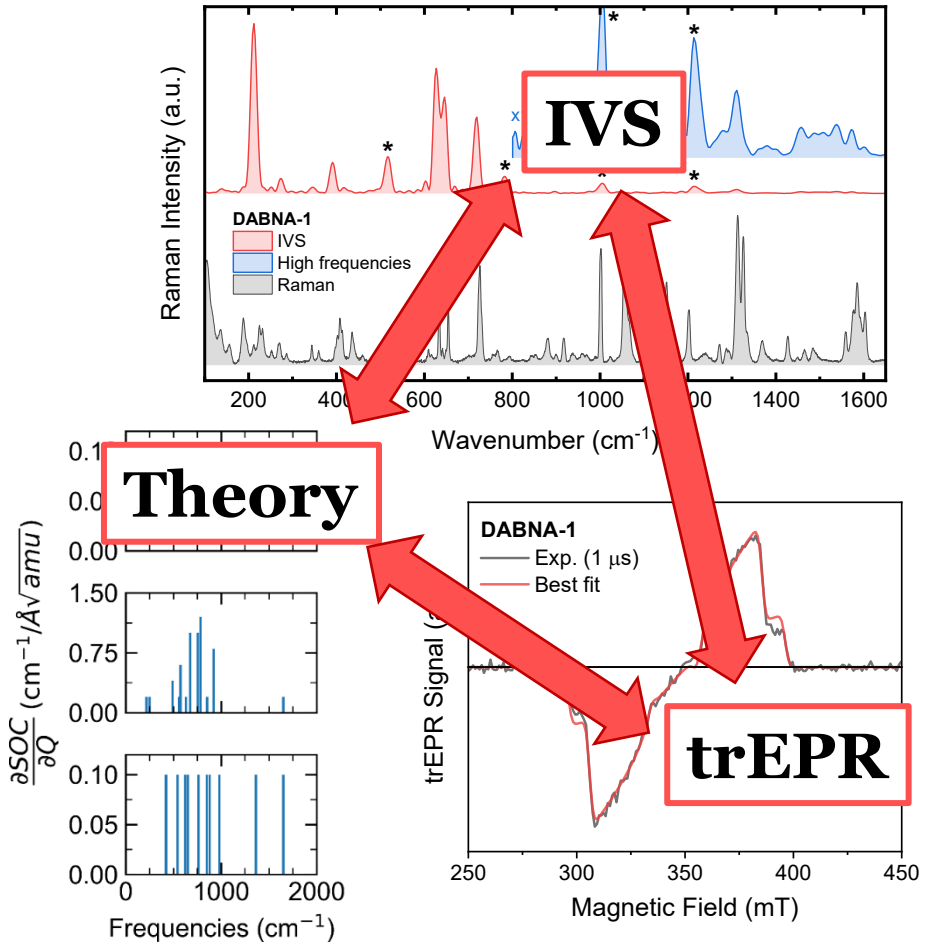


$p_x = 0$ $p_y = 0.70$ $p_z = 0.30$

Unpublished work

A complete picture of ISC





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Prof Vladimir Dyakonov

University of Oxford

Dr Alberto Privitera (now U. Florence)
Dr William Myers
Prof Moritz Riede

University of California, Santa Barbra

Dr Akchheta Karki
Prof Thuc-Quyen Nguyen

University of Namur

Dr Danillo Valverde
Dr Gaetano Ricci
Prof Yoann Olivier

Linköping University

Dr Deping Qian (now Strait Institute)
Prof Feng Gao

Central South University

Dr Jun Yuan

Swedish Research Council

Knut and Alice Wallenberg Foundation

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