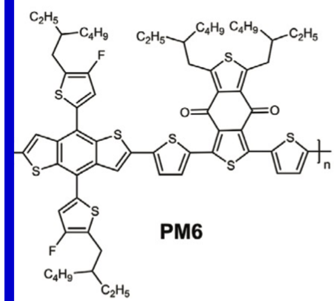
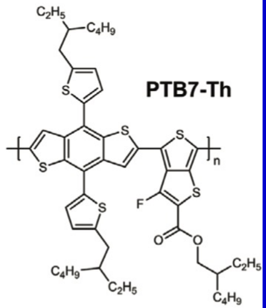
Efficiency-Limiting Pathways in NFA-based Organic Solar Cell Blends – A Triplet Story

Vladimir Dyakonov
University of Würzburg, Germany

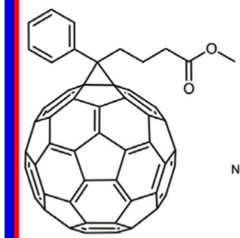
Donor



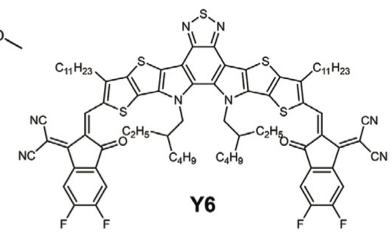
PM6



PTB7-Th



$PC_{60}BM$

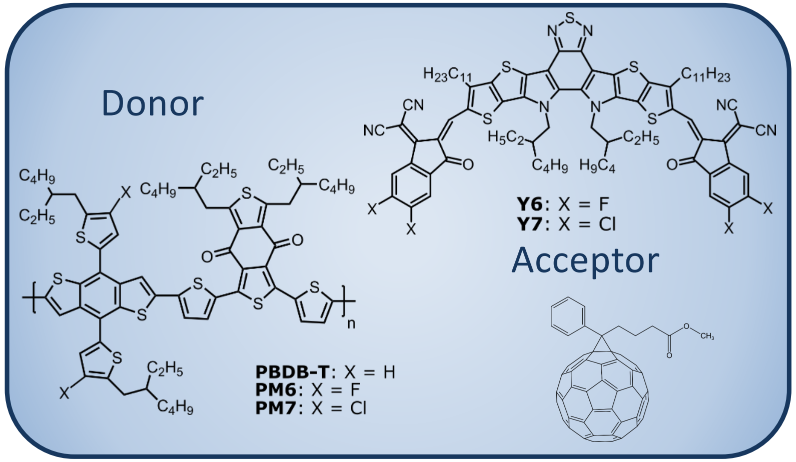


Y6

non-fullerene

Acceptor

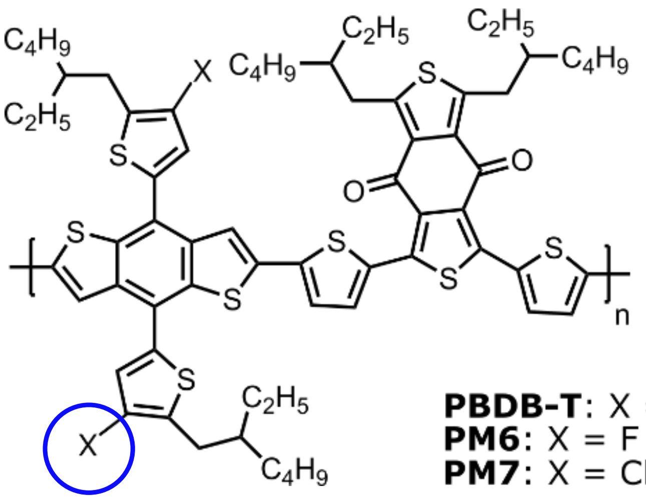
Donor-Acceptor Blends



- Non-fullerene acceptors (NFAs) have enabled power conversion efficiencies > 19% in organic solar cells
- However, the open-circuit voltage remains low relative to their optical gap due to excessive non-radiative recombination. **Can we identify them?**

Donor-Acceptor Blends

Donor



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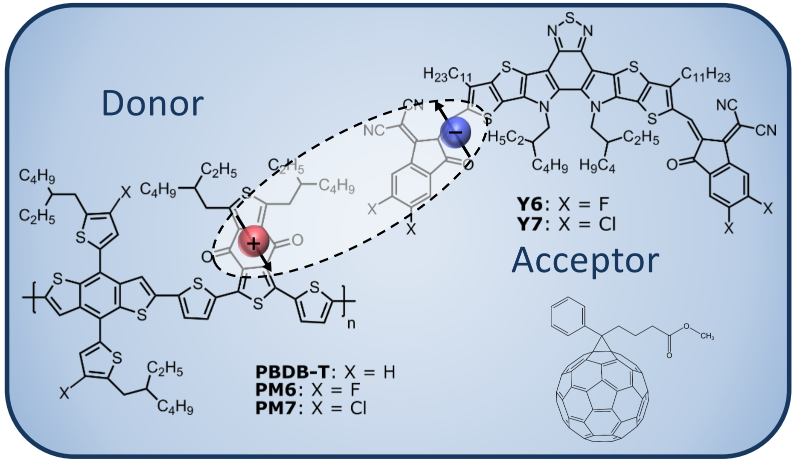
Donor-Acceptor Blends

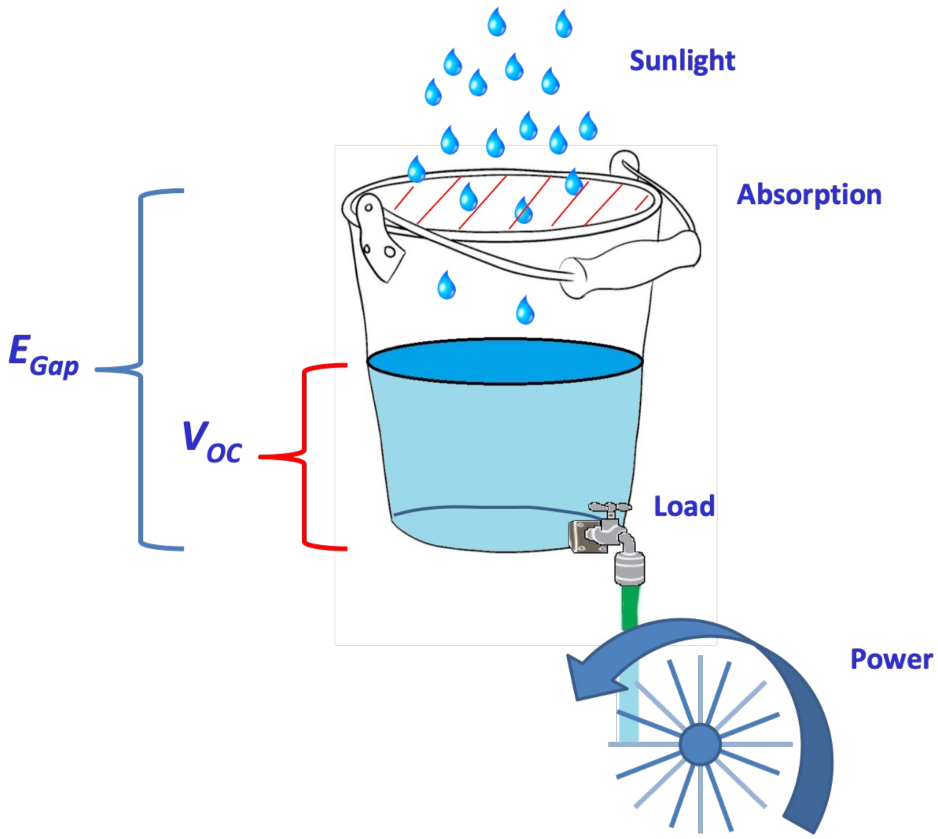


$$\Delta V_{nr} = -\frac{k_B T}{q} \cdot ln(EQE_{EL})$$

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

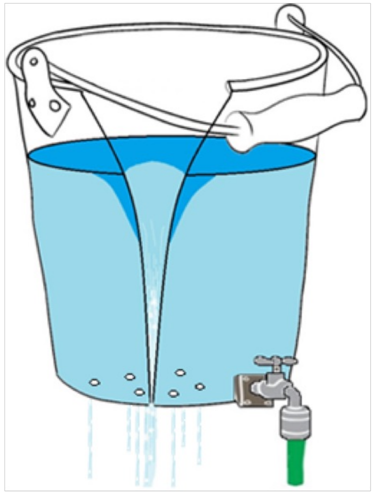
χ – *the fraction of radiative recombination events (spin-singlet excitations)*

PV Bucket Analogy



Solar Cells Simplified

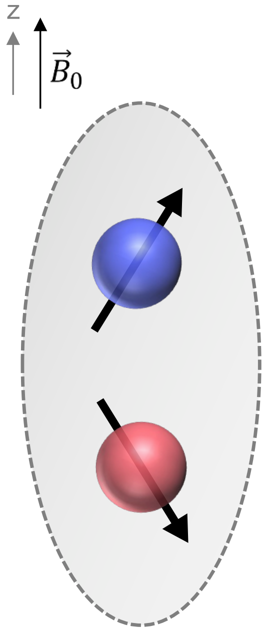
"All solar cells have recombination losses"
= "All buckets must have holes"!



…most buckets have too many holes…

Spin-States

Spin States: $|\psi_S\rangle = |S, M_S\rangle$



Singlet State (S = 0)

$|S\rangle = |0,0\rangle = 1/\sqrt{2}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$

Triplet States (S = 1)

$|T_+\rangle = |1,1\rangle = |\uparrow\uparrow\rangle$

$|T_0\rangle = |1,0\rangle = 1/\sqrt{2}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$

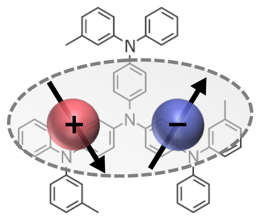
$|T_-\rangle = |1,-1\rangle = |\downarrow\downarrow\rangle$

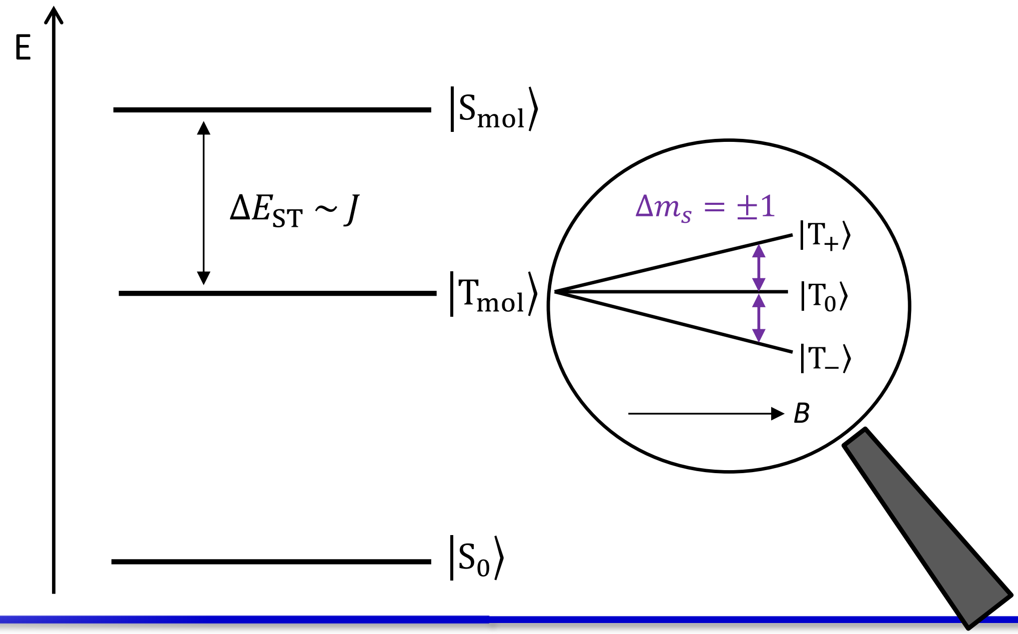
Hamilton Operator:

$$\hat{H} = \hat{H}_{EX} + \hat{H}_{EZ} + \hat{H}_{ZFS} = \hat{\vec{S}}_1^T \boldsymbol{J}\, \hat{\vec{S}}_2 + \boldsymbol{g}\, \mu_B\, \hat{\vec{S}}\, \vec{B} + \hat{\vec{S}}^T \boldsymbol{D}\, \hat{\vec{S}}$$

$\sim$ overlap $\psi_{HOMO} \leftrightarrow \psi_{LUMO}$

Molecular State





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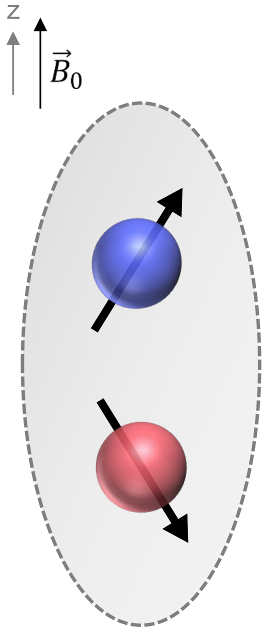

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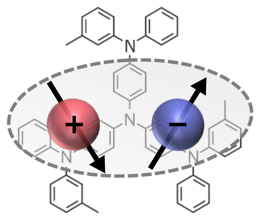
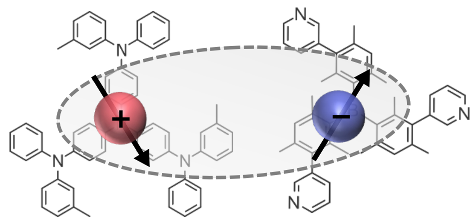
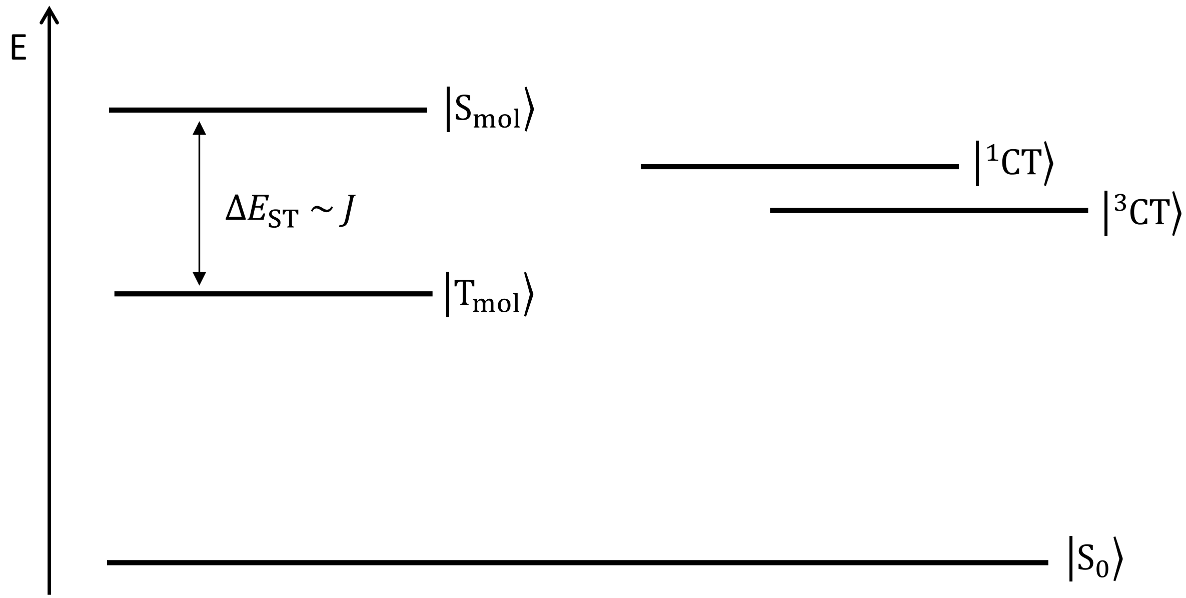


Charge Transfer State (CT)





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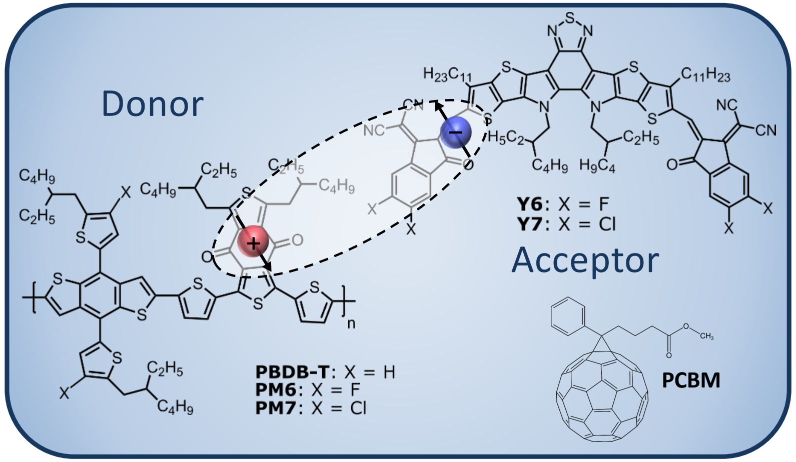
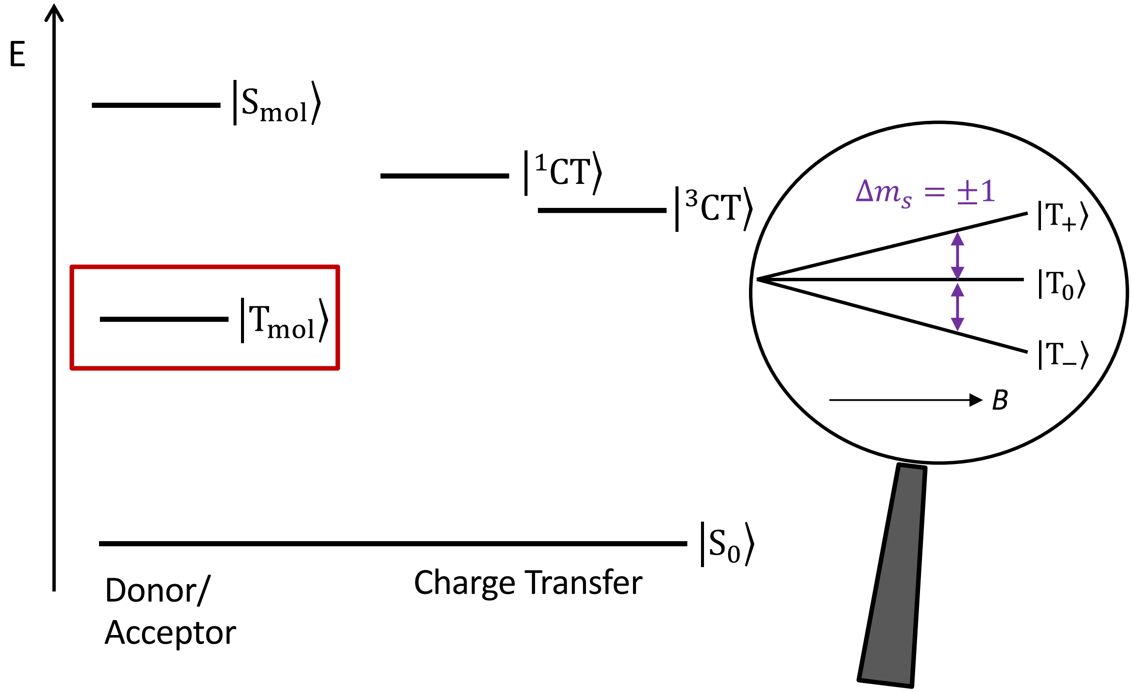
$\sim$ overlap $\psi_{\text{HOMO}} \leftrightarrow \psi_{\text{LUMO}}$

Spin-States involved in OPV

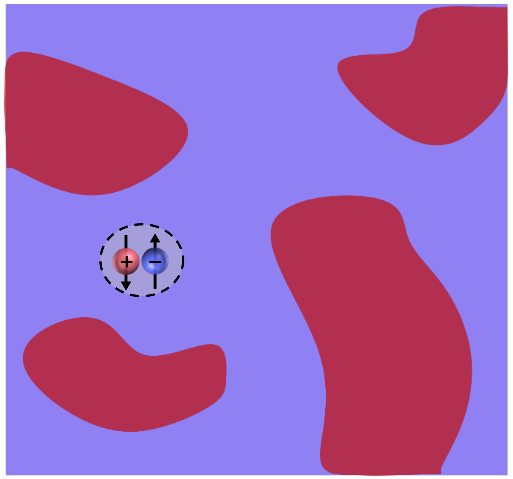
Organic Photovoltaics

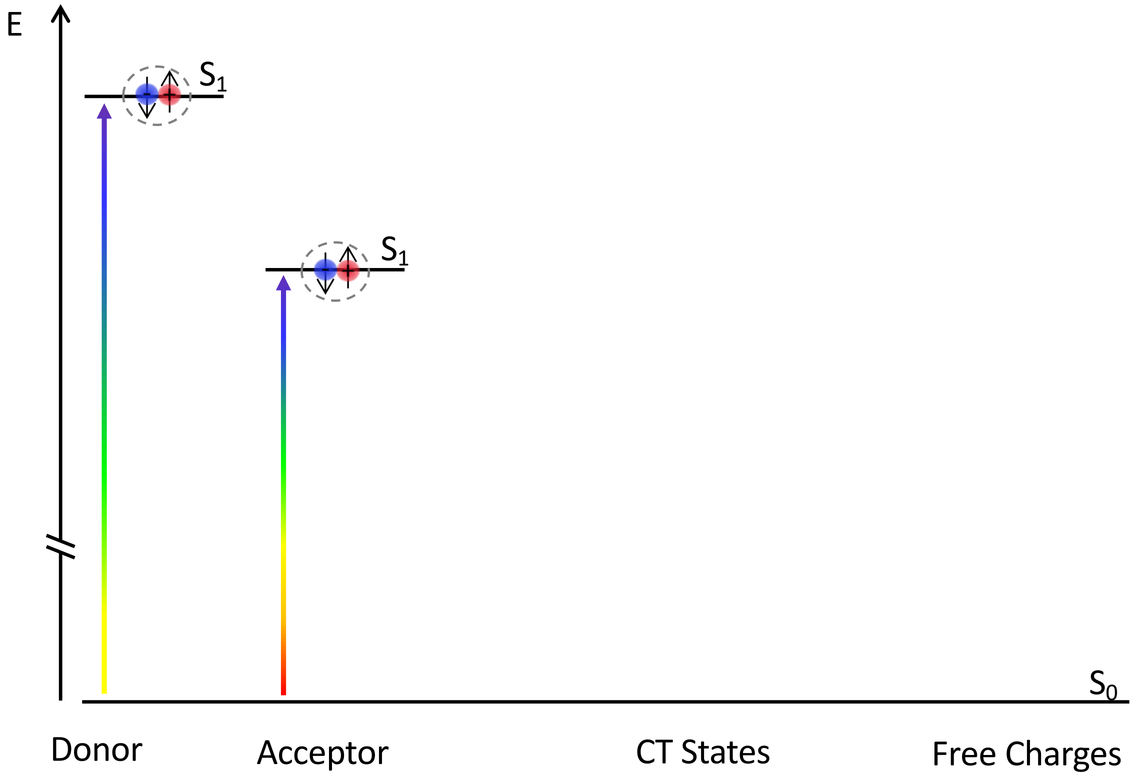




→ triplet states, pathways, kinetics?

Triplet Excitons in OPV Blends





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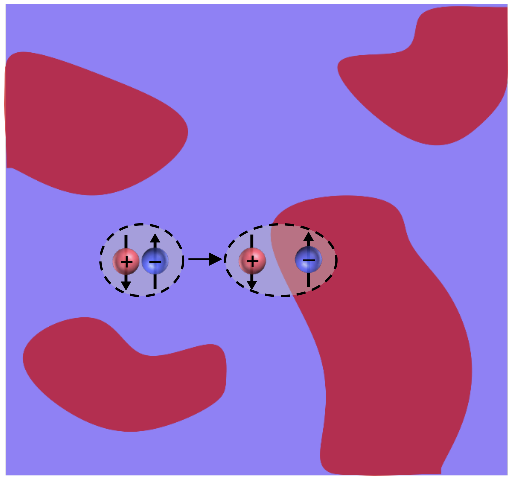

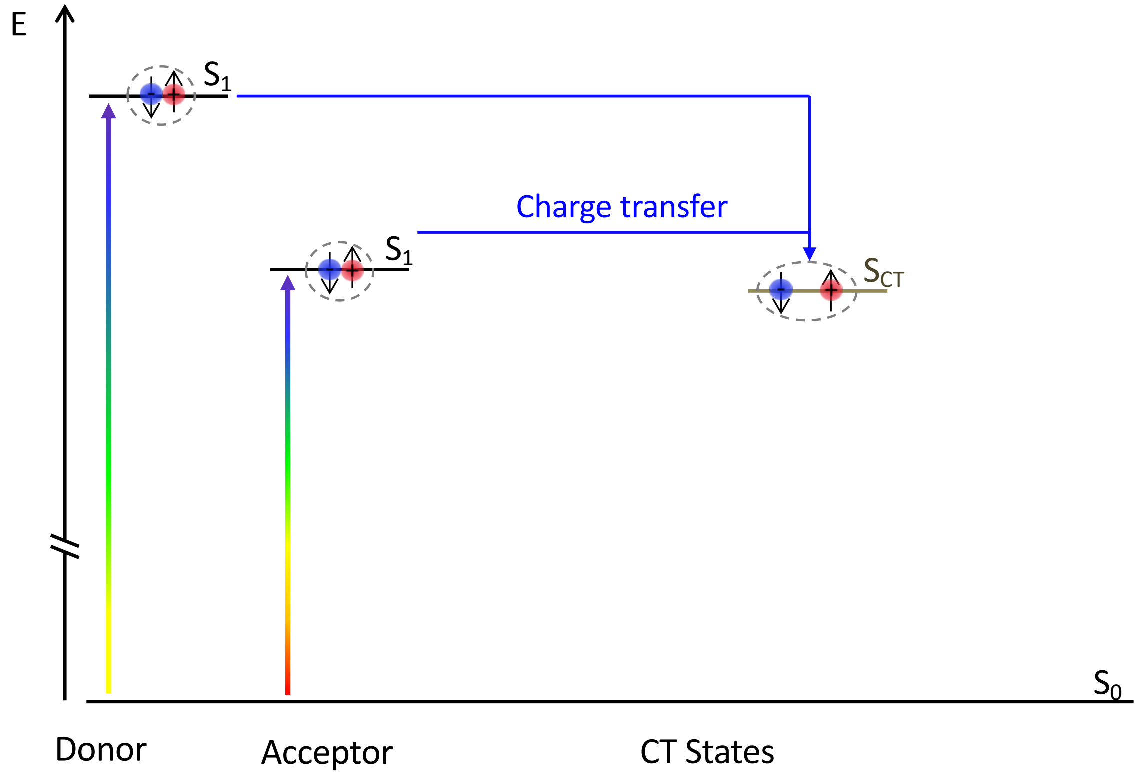

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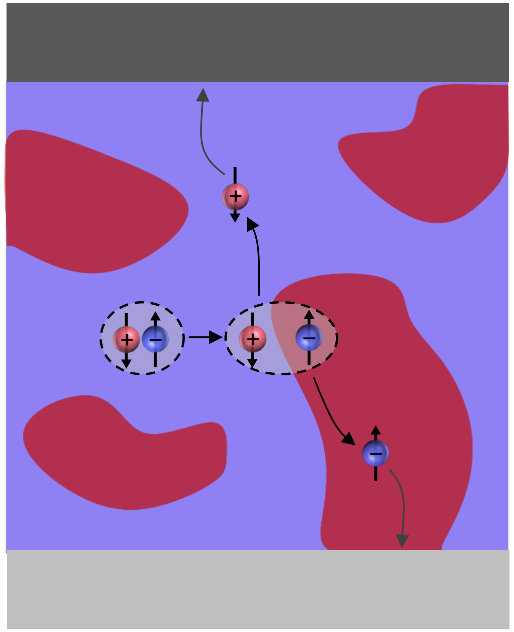

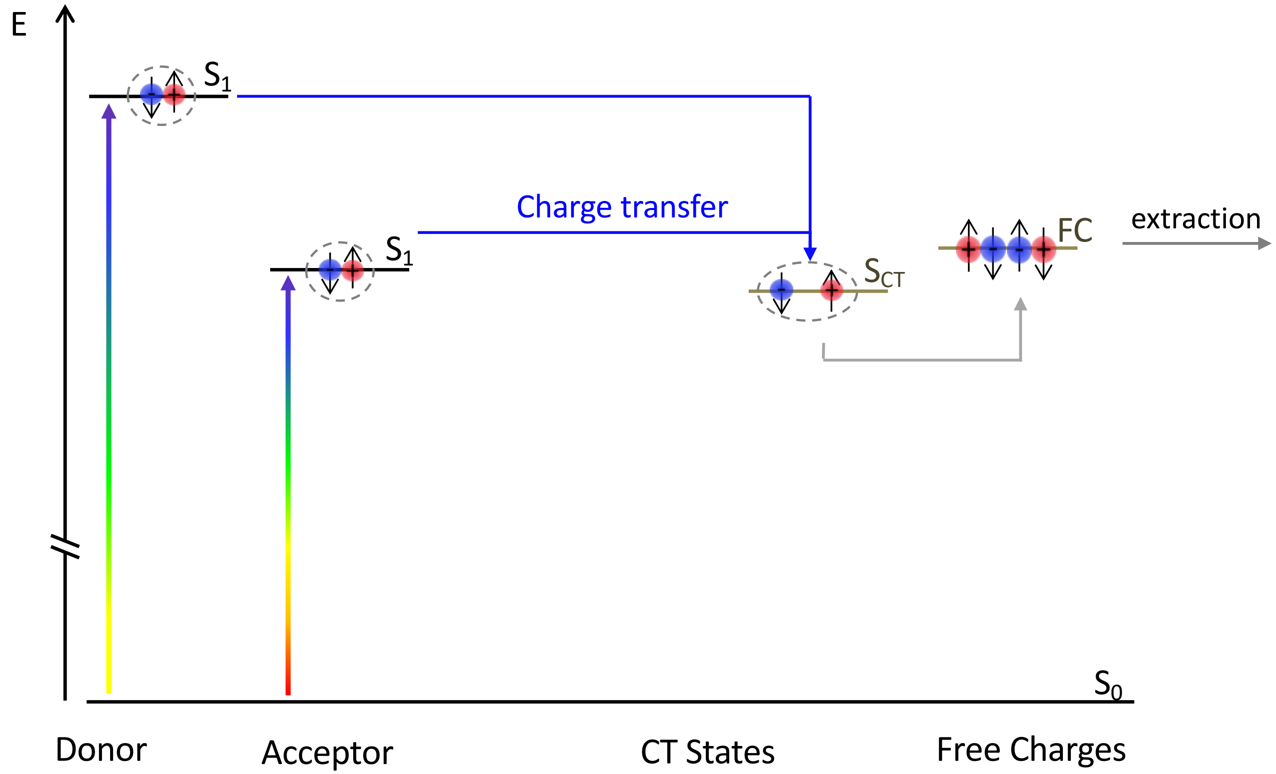

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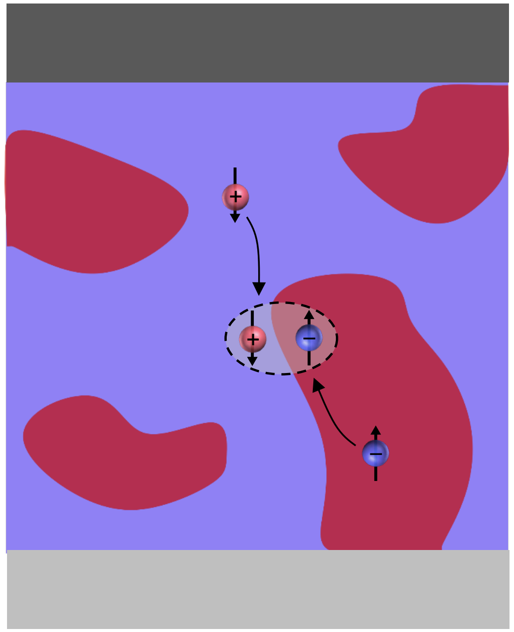

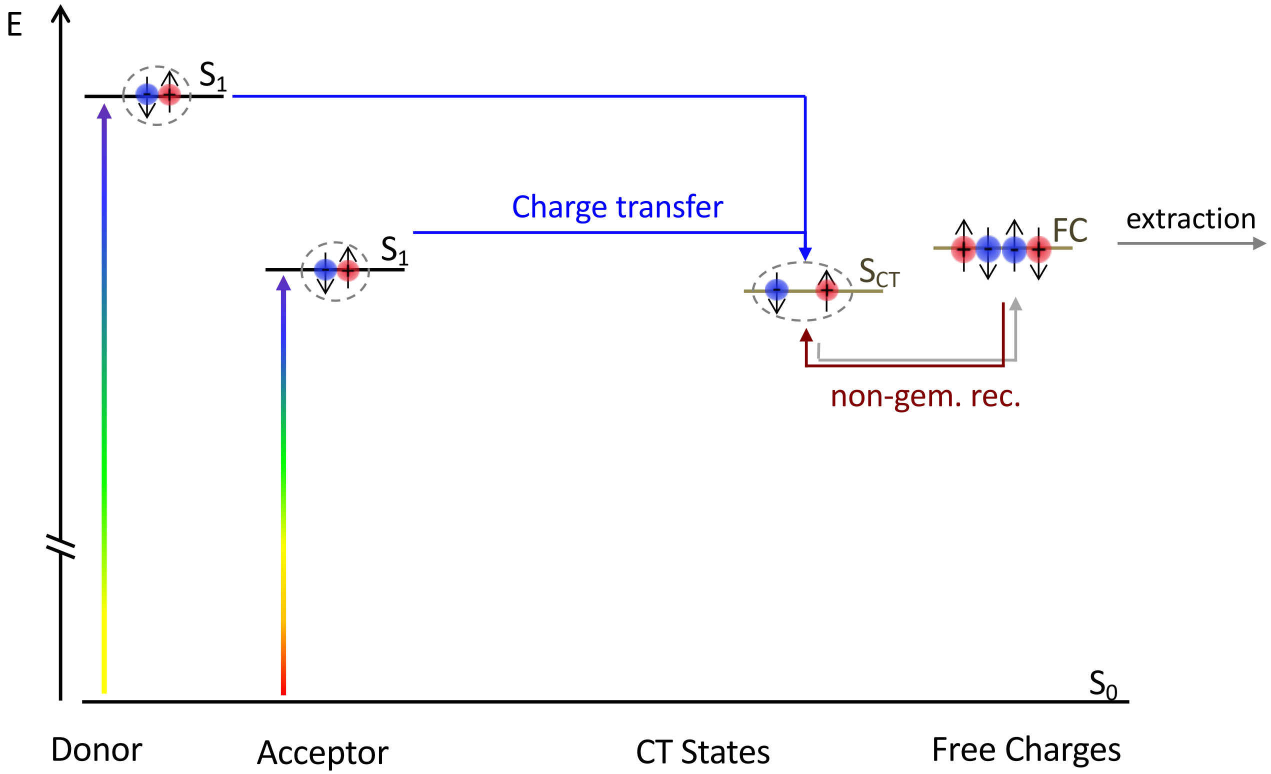

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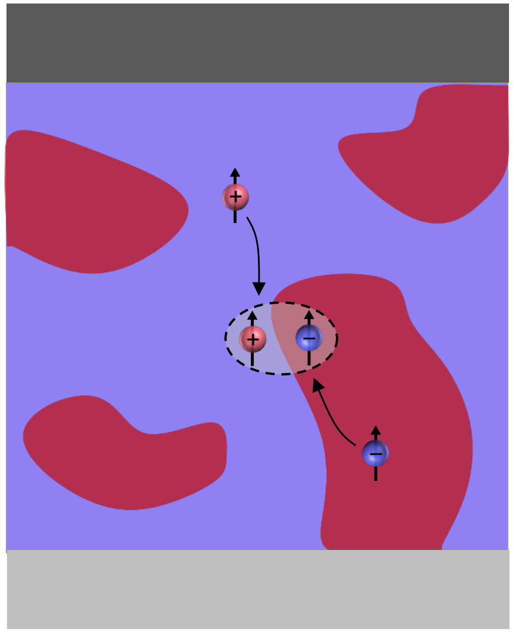
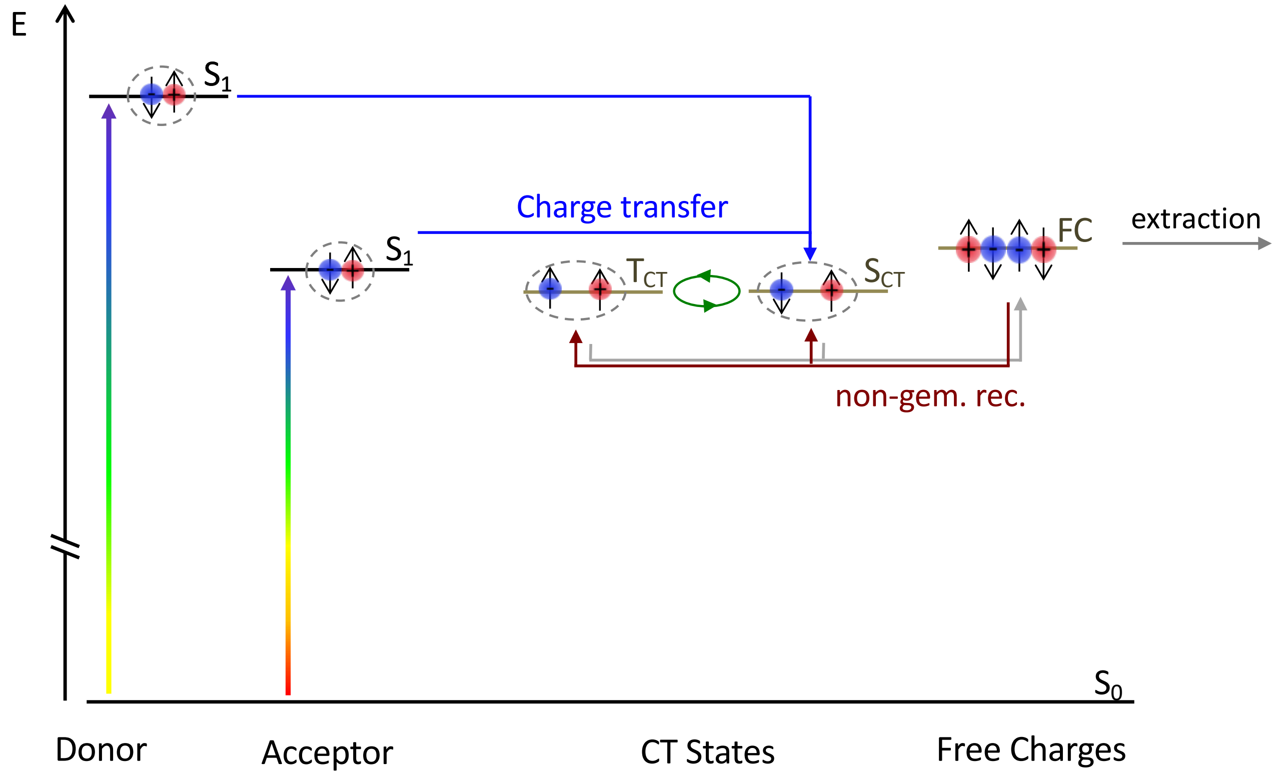
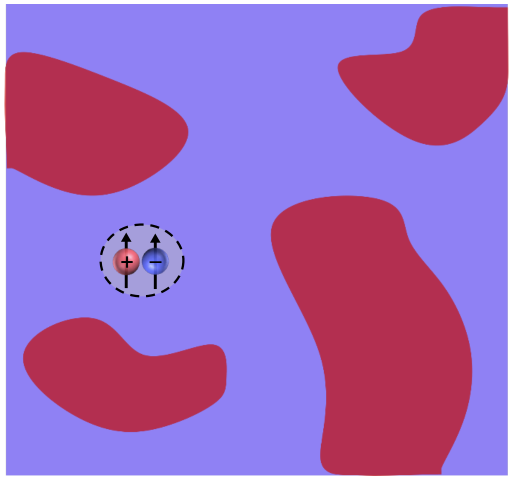
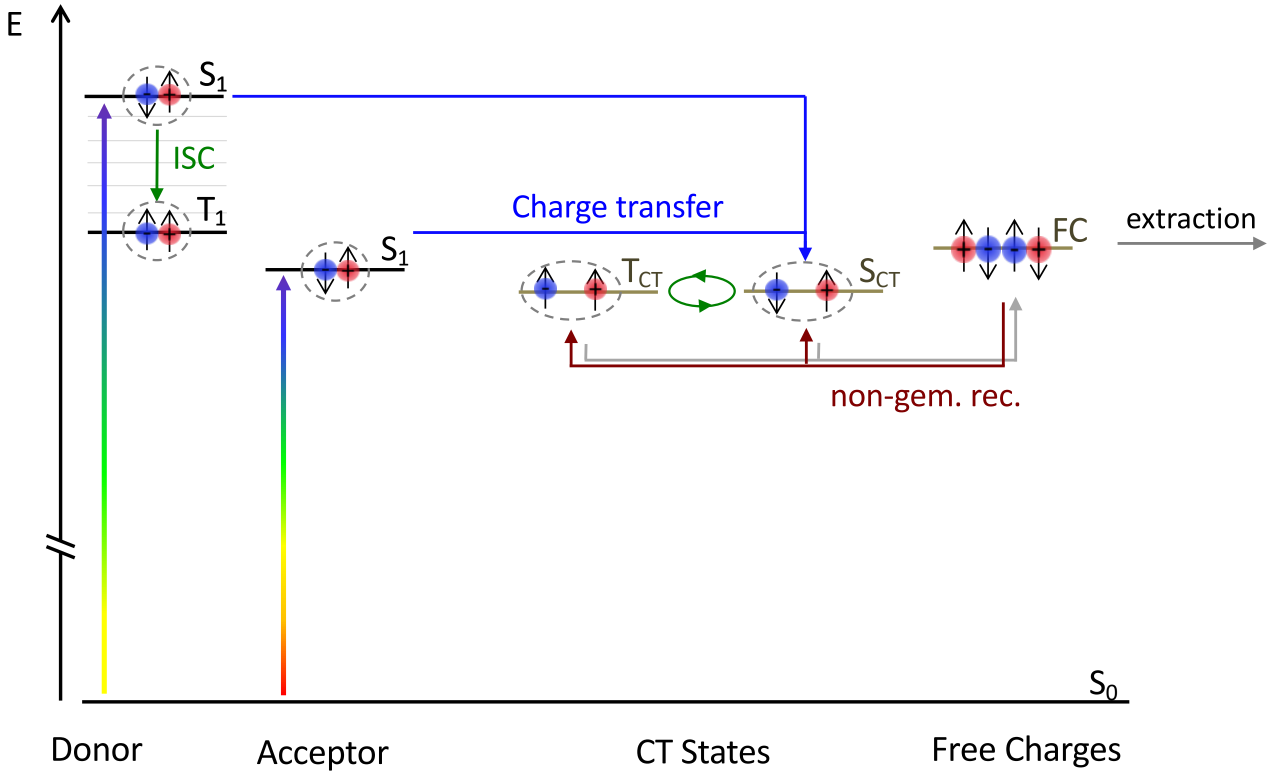




Triplet Excitons in OPV Blends





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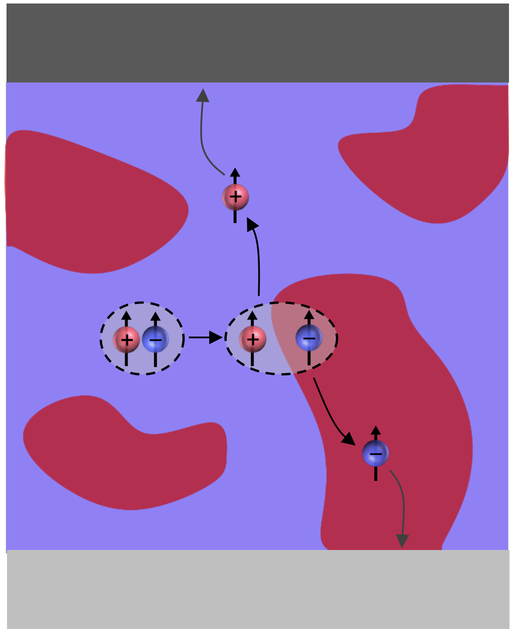

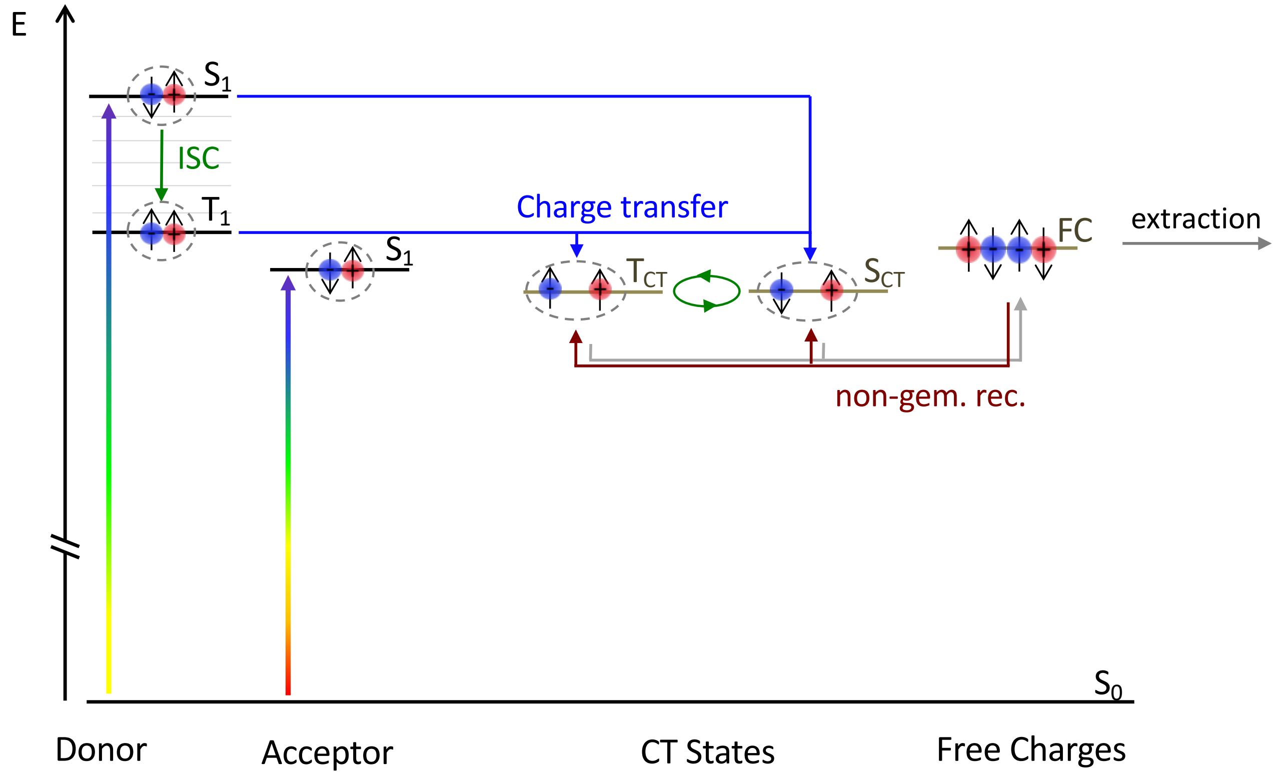

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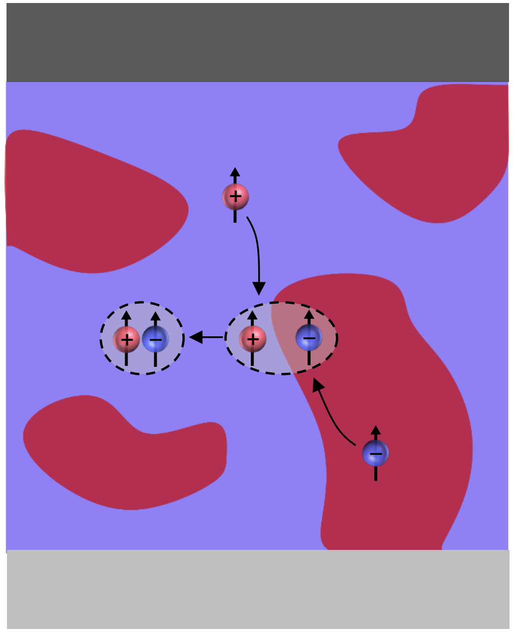
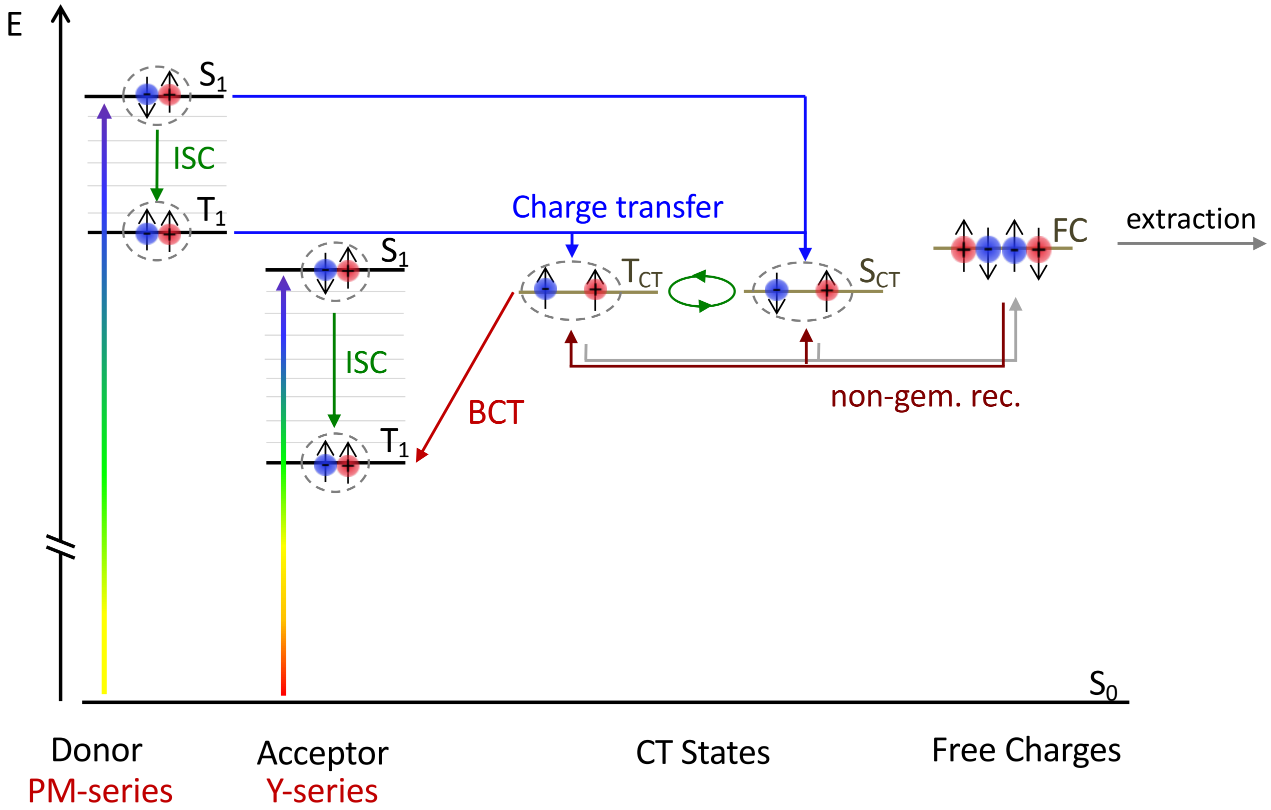
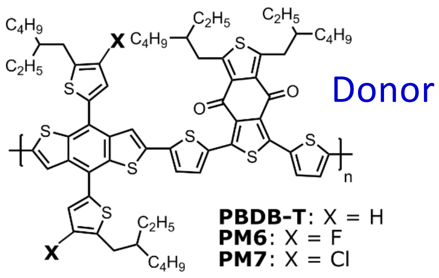
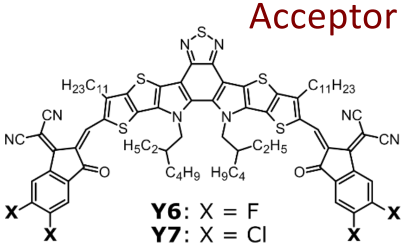


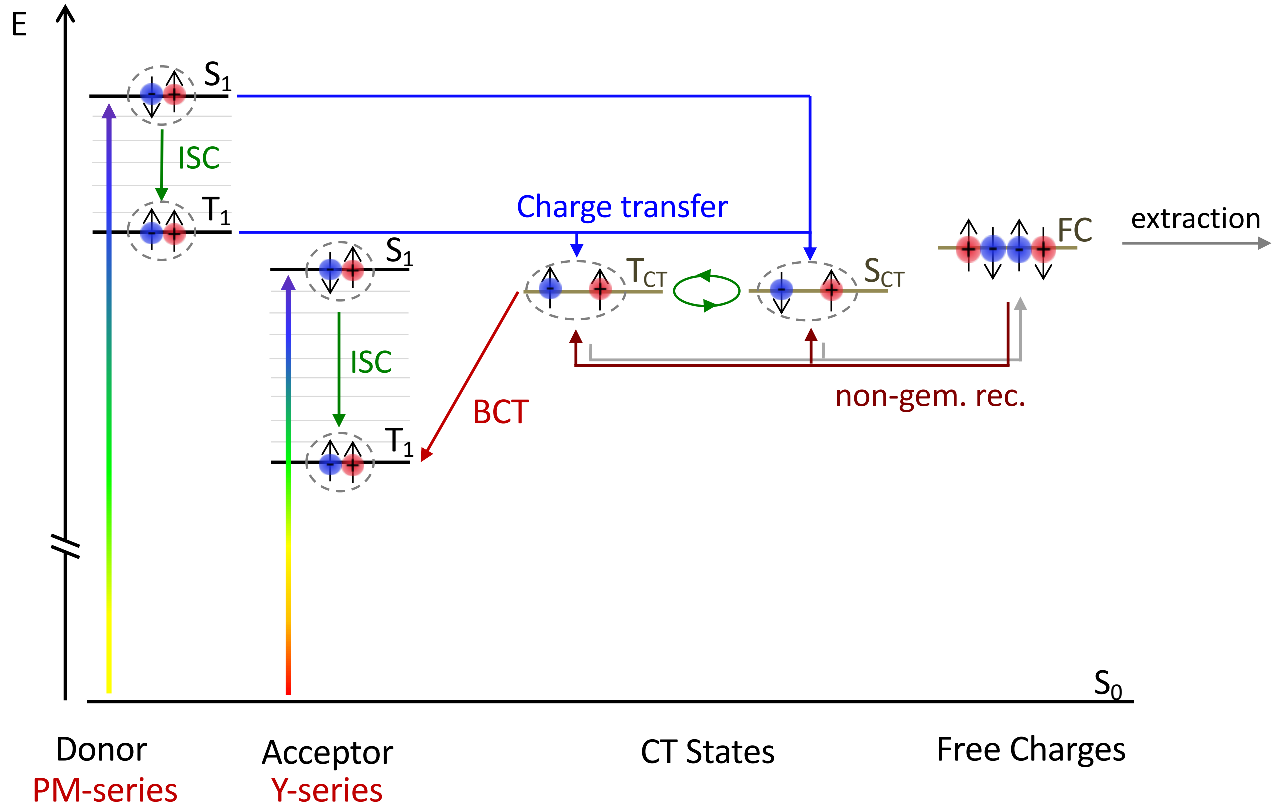


Back Charge Transfer (Electron- / Hole- Back Transfer)

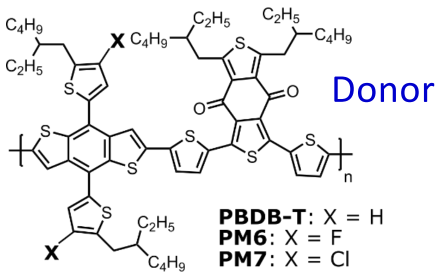
Triplet Excitons in NFA Blends

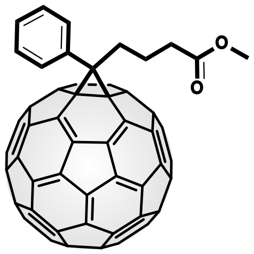




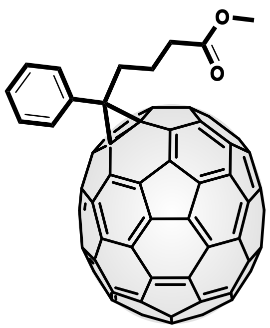


Triplet Excitons in Fullerene Blends

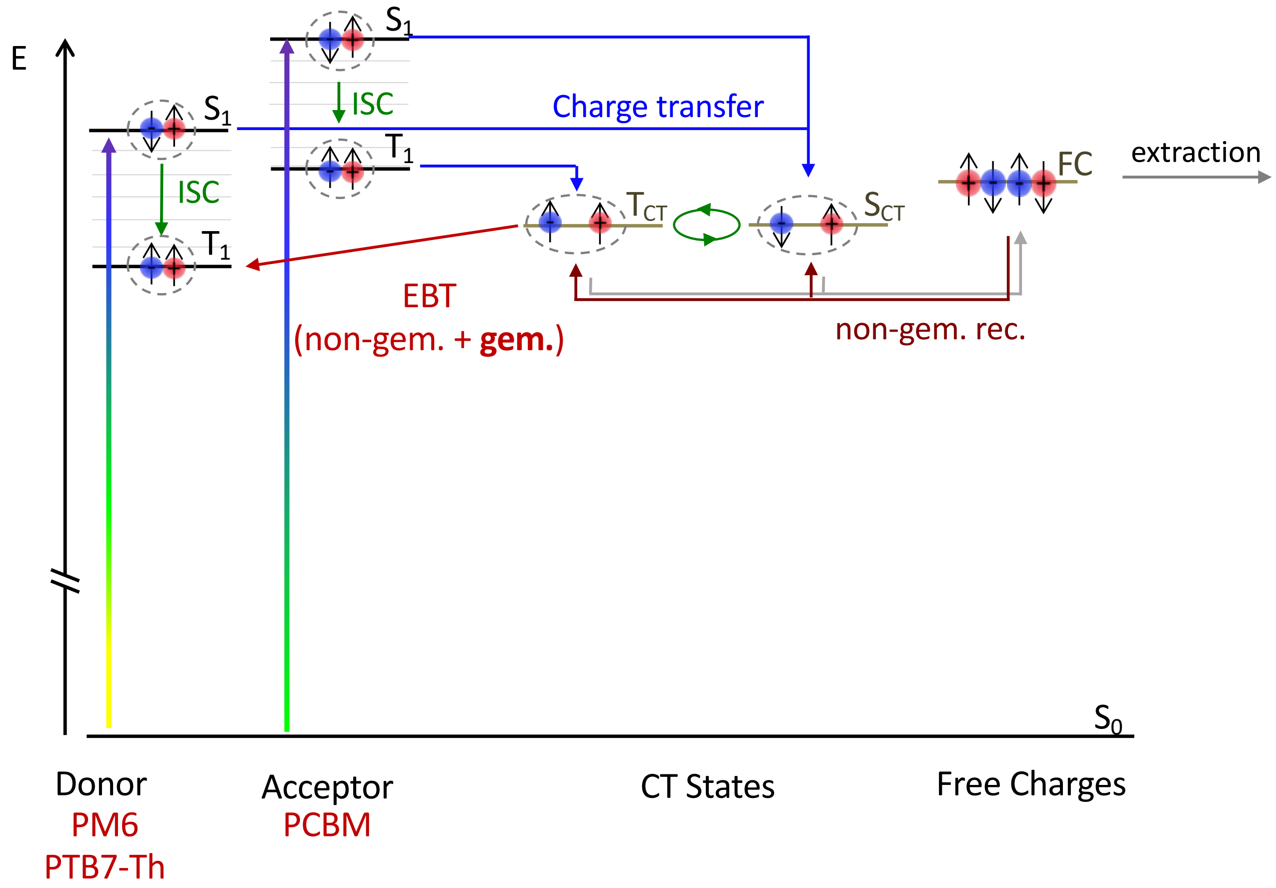




PC$_{60}$BM

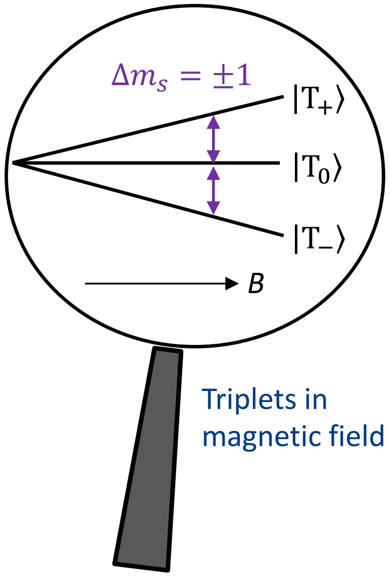


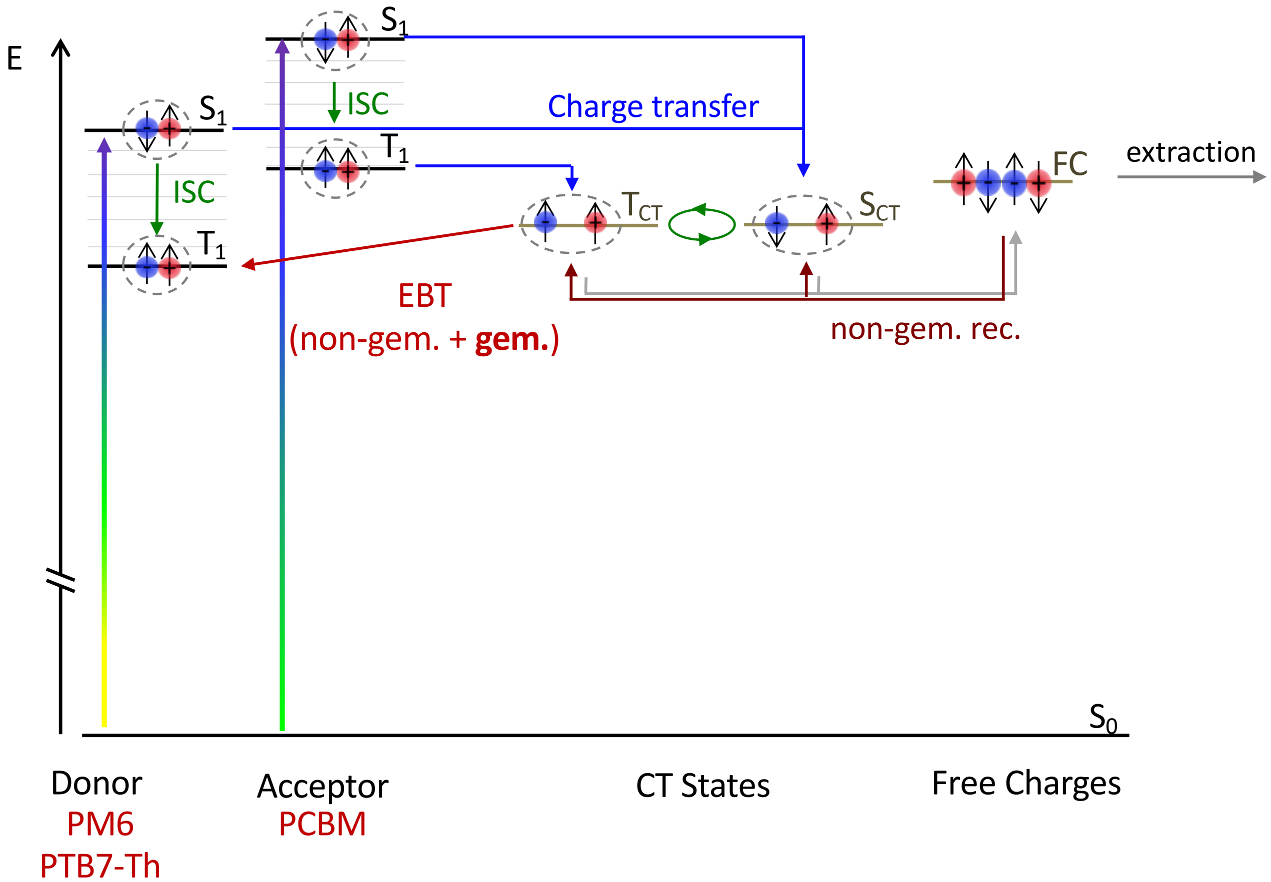
PC$_{70}$BM



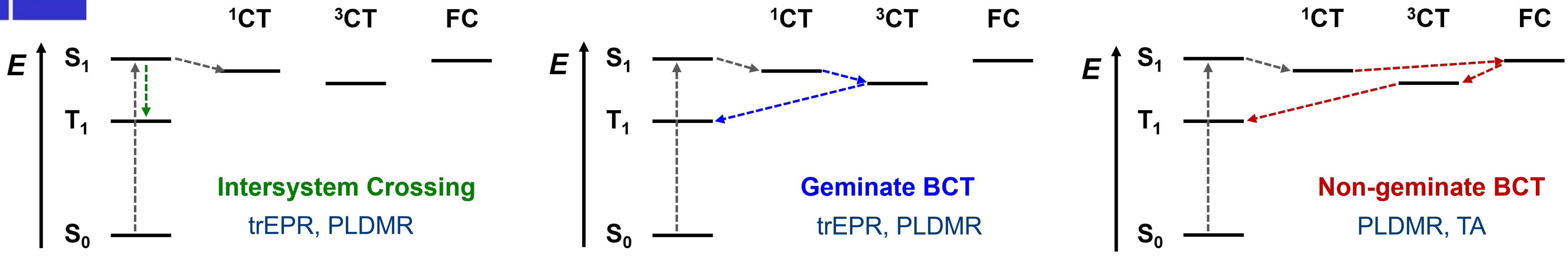
Triplet Excitons in Fullerene Blends

→ **how to detect triplets**
and distinguish all these pathways?
→ **„toolbox“ of spin-sensitive spectroscopy**



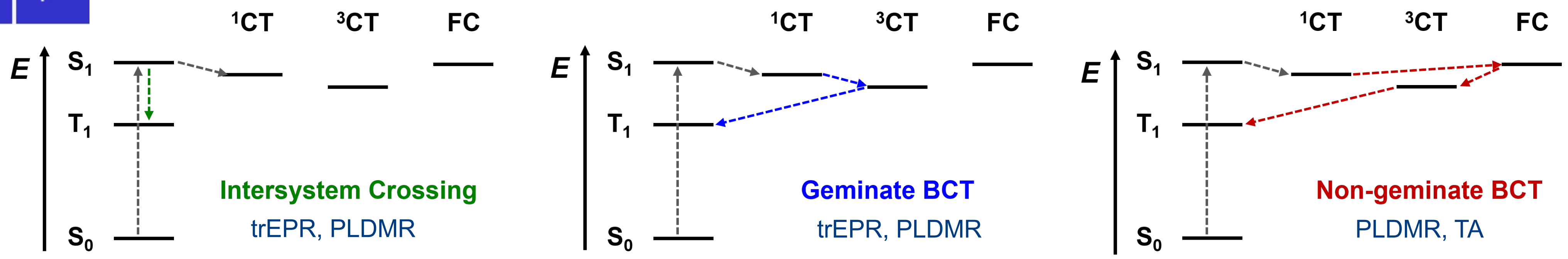


Toolbox for detecting and assigning triplet pathways



Toolbox for detecting Triplets
Adv. Energy Mater. 2022
10.1002/aenm.202103944

Toolbox for detecting and assigning triplet pathways



trEPR – Transient Electron Paramagnetic Resonance	**TA – Transient Absorption**
+ distinguish between mechansism (spin polarization) + time resolution (ns to µs) + detects also triplet excitons not participating in luminescence	+ time resolution (fs to ms) + quantitative + room temperature sensitive

PLDMR – PL Detected Magnetic Resonance

+ highest sensitivity – detects all triplets (also minor pathways)
+ ISC / (non-) gem. BCT

Toolbox for detecting Triplets
Adv. Energy Mater. 2022
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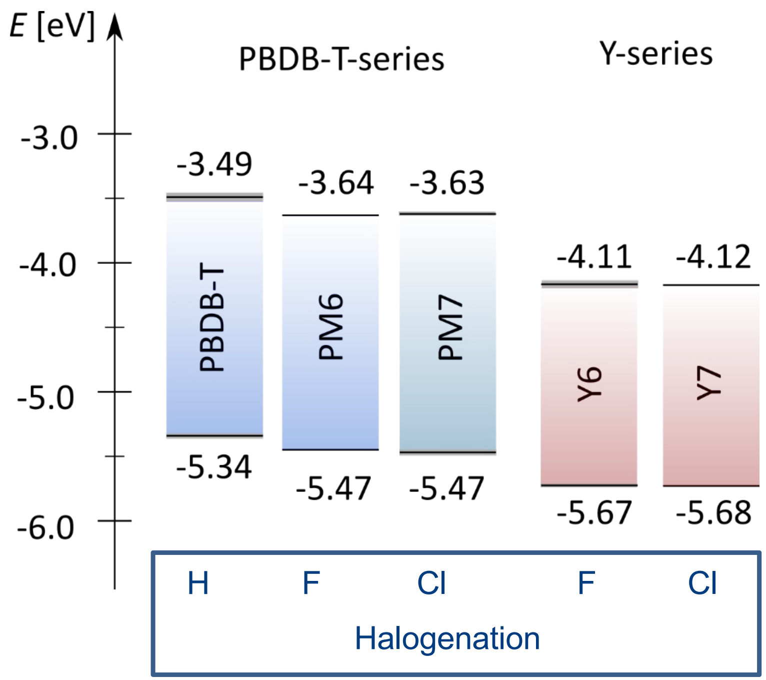
Energetics of halogenated D:A blends

HOMO/LUMO level



Singlet, Triplet and CT States

Material	S_1 [eV]	ΔE_{ST} [eV]	T_1, T_2 [eV]	CT [eV]
PBDB-T	1.85	0.40	1.45	
PM6	1.92	0.41	1.51	
PM7	1.92	0.41	1.51	
Y6	1.39	0.56, 0.35	0.83, 1.04	
Y7	1.40	0.55, 0.34	0.85, 1.06	
PBDB-T:Y6				1.35
PM6:Y6				1.37
PM7:Y6				1.37
PBDB-T:Y7				1.36
PM6:Y7				1.38
PM7:Y7				1.38

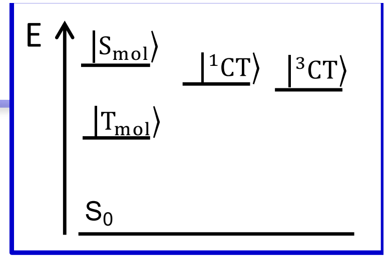
ΔE_{ST} calculated, T_1, T_2 determined by substracting ΔE_{ST} from S_1

G. Londi, Mons, Belgium

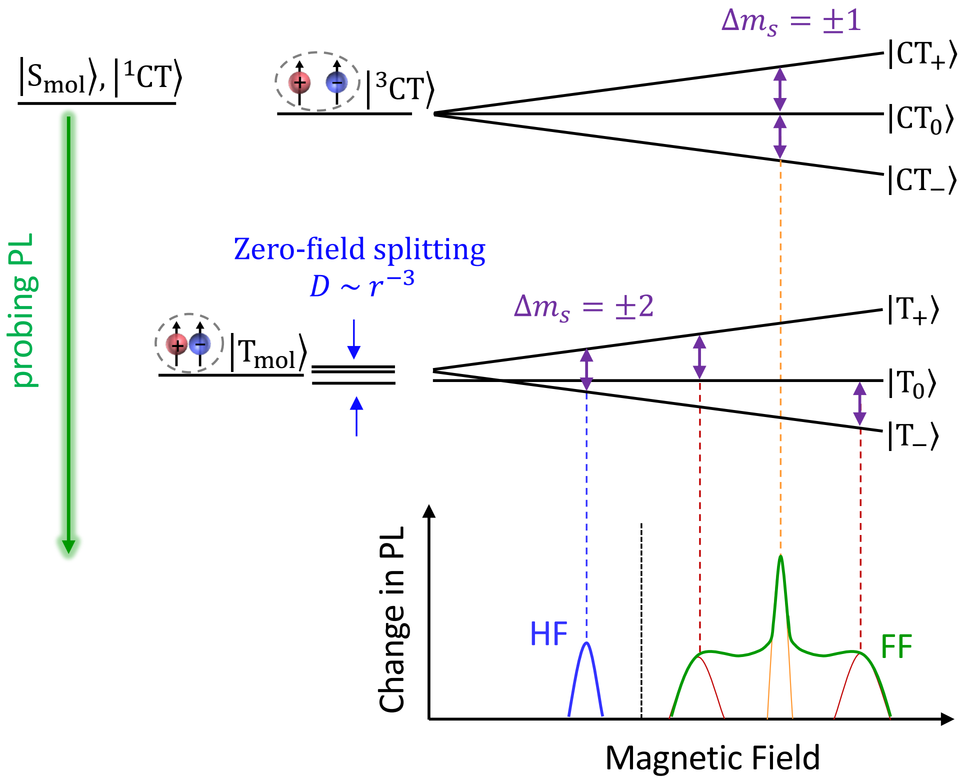
Influence of halogenation:
→ similar energetics
→ improved PCE

Halogenation and Triplets
Adv. Funct. Mater. 2023
10.1002/adfm.202212640

Triplet Excitons in OPV Blends



Photo**l**uminescence **D**etected **M**agnetic **R**esonance



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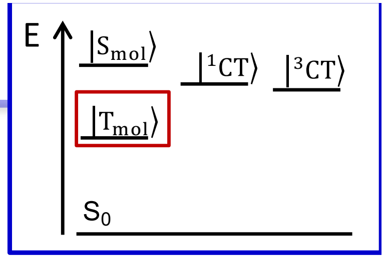
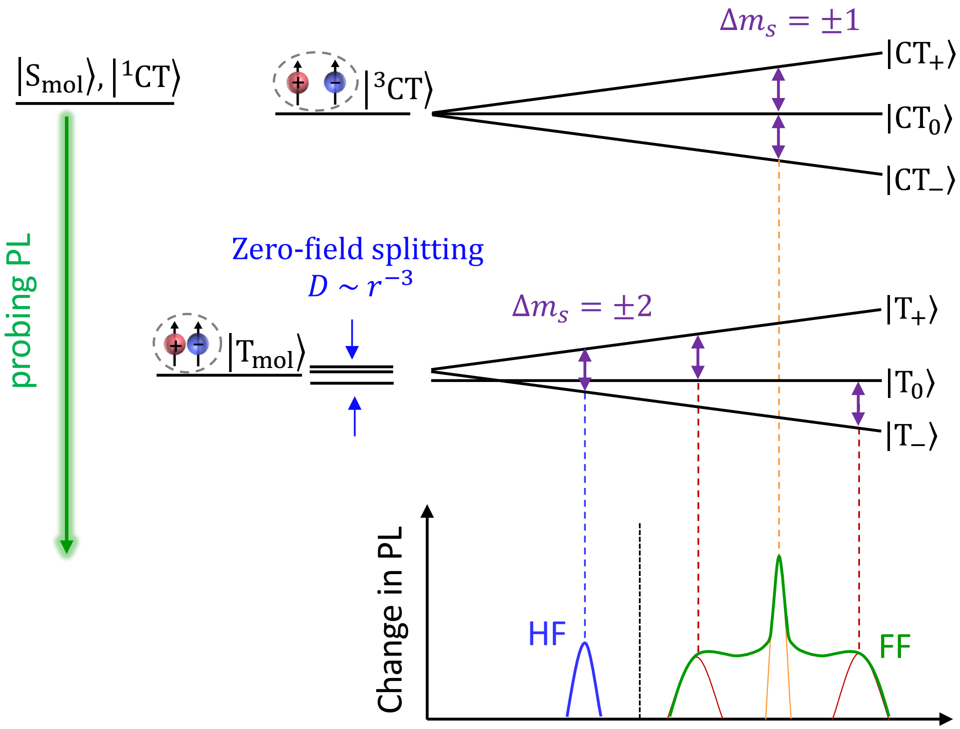
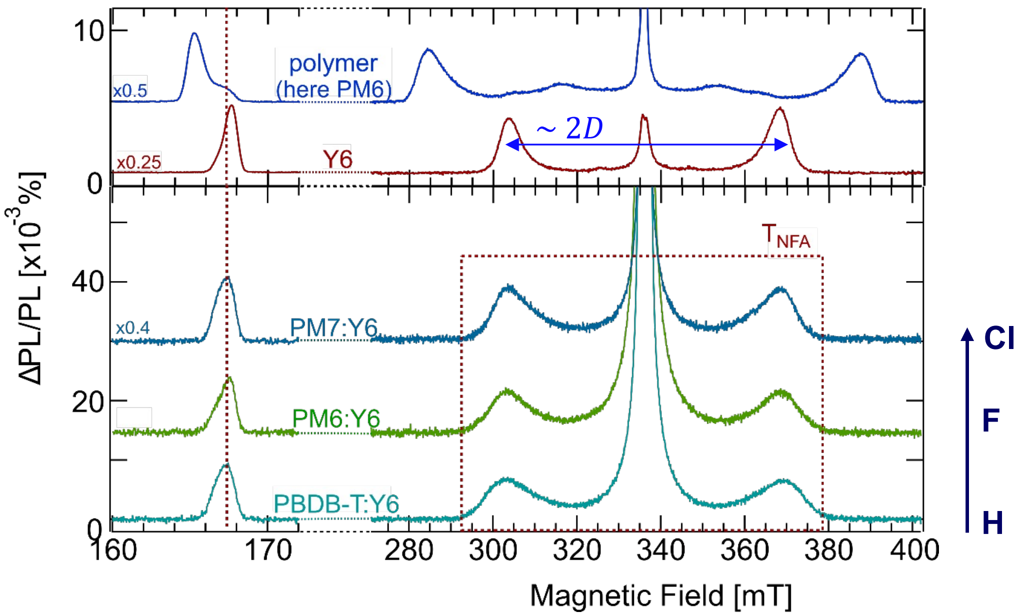
Triplet Excitons in OPV Blends

Photoluminescence Detected Magnetic Resonance





Triplet Excitons in PLDMR



→ Triplets in all blends on Y-series acceptor!

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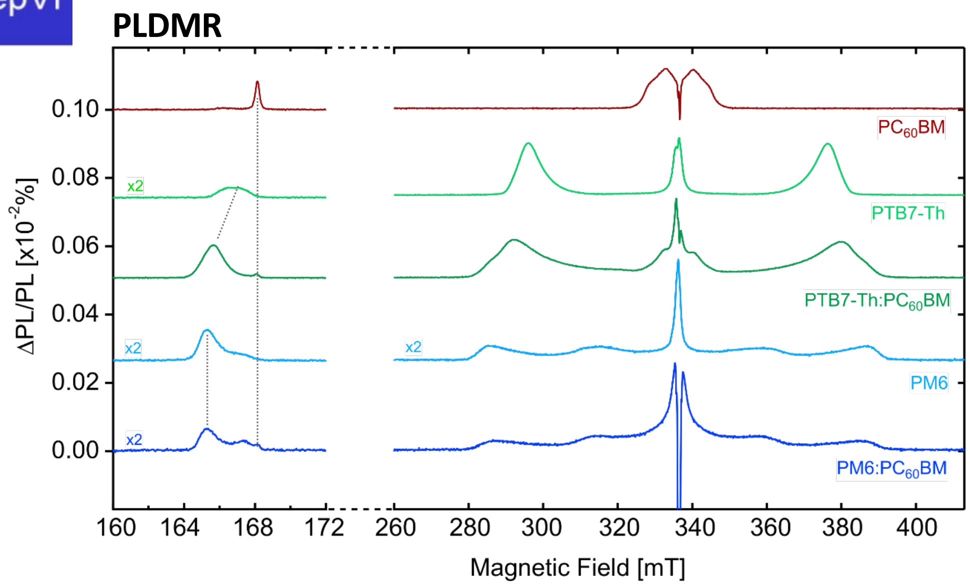
10.1002/adfm.202212640

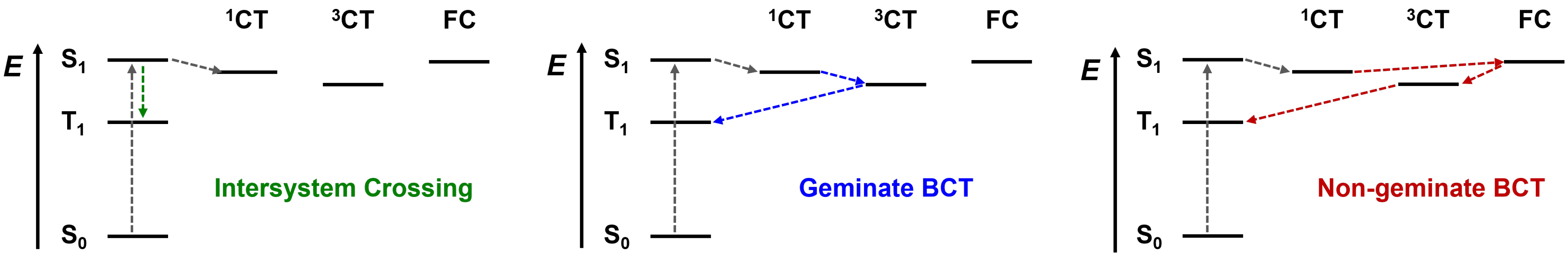
Fullerene based OPV – PLDMR



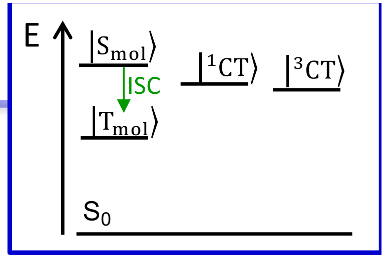
→ Triplets on donor

→ Small portion of triplets also on fullerene (domains)

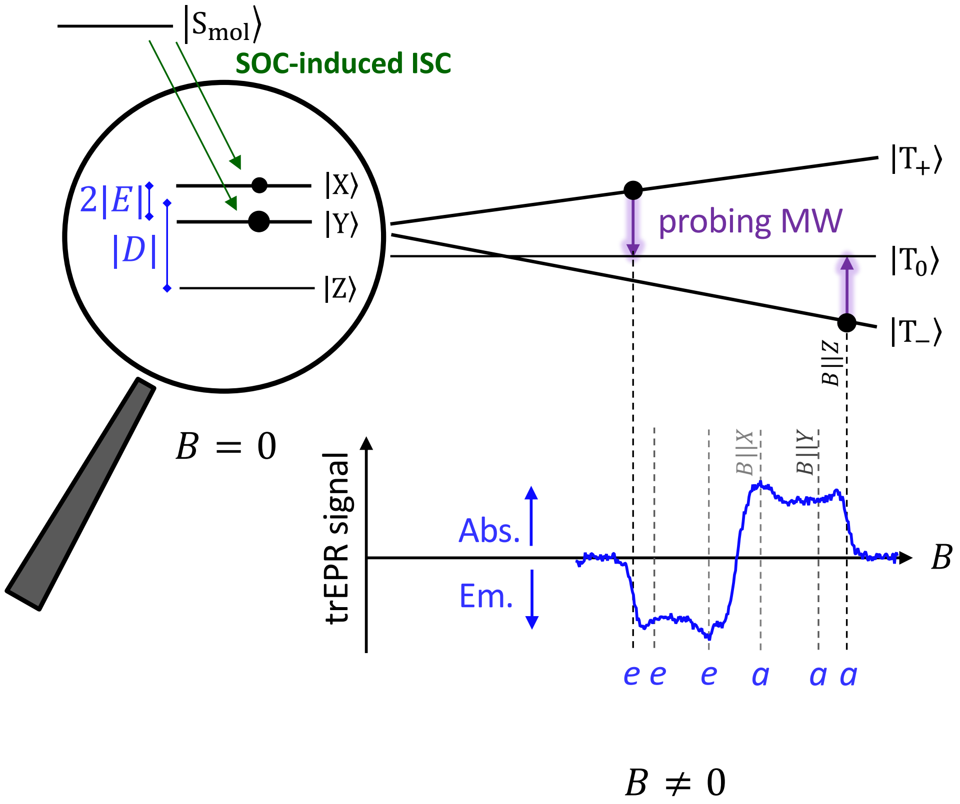
How were they formed (3 options) ?



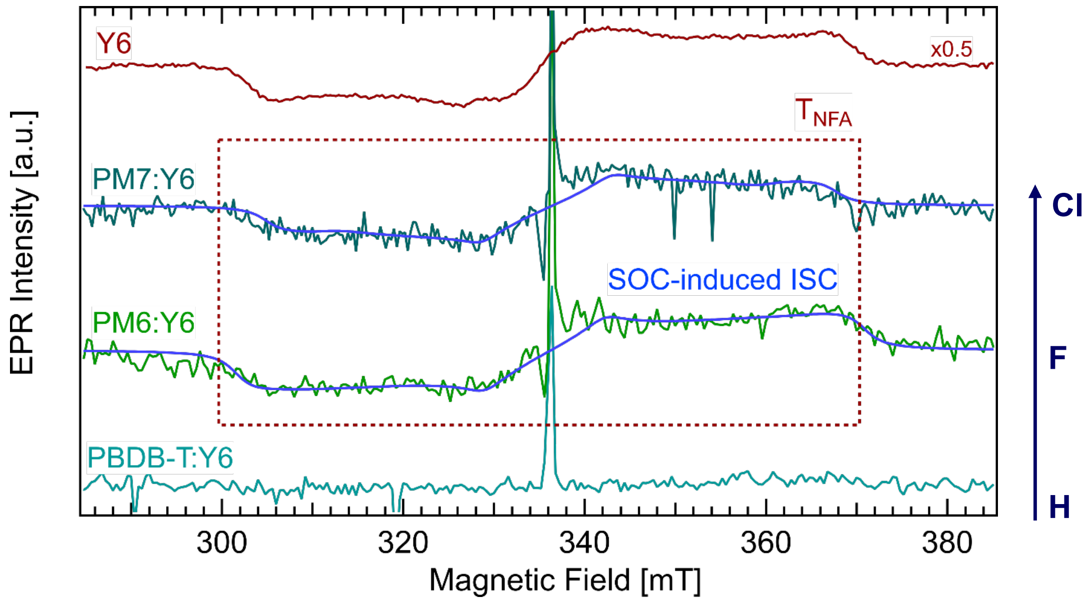
Triplet Excitons in OPV Blends



Transient EPR



Pathway by trEPR



→ triplet excitons on Y6 by SOC-induced ISC

→ no Y6 Triplets in PBDB-T:Y6

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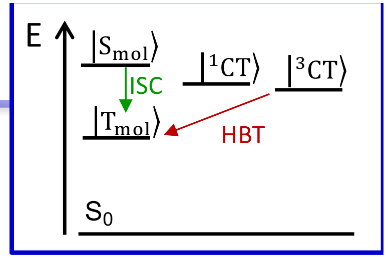
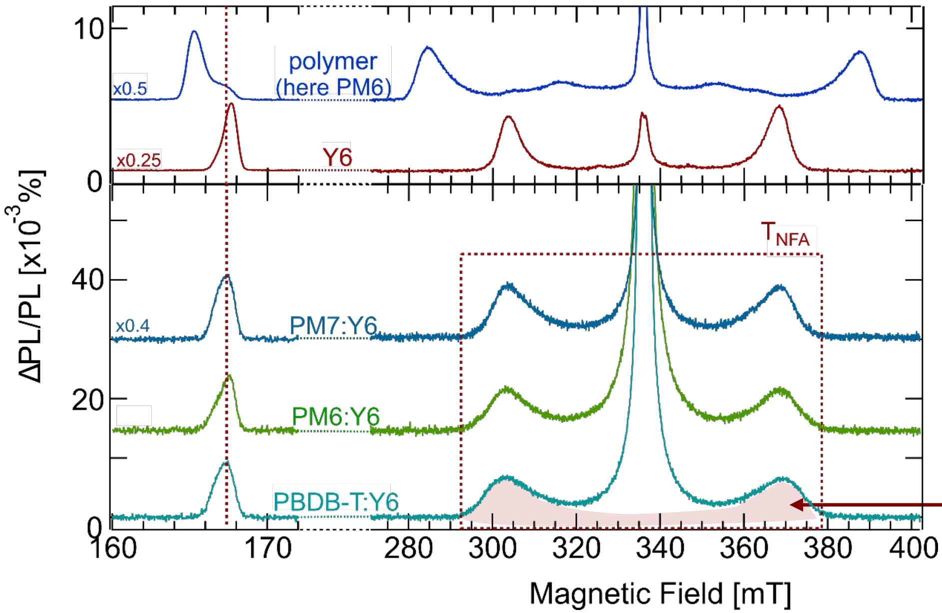
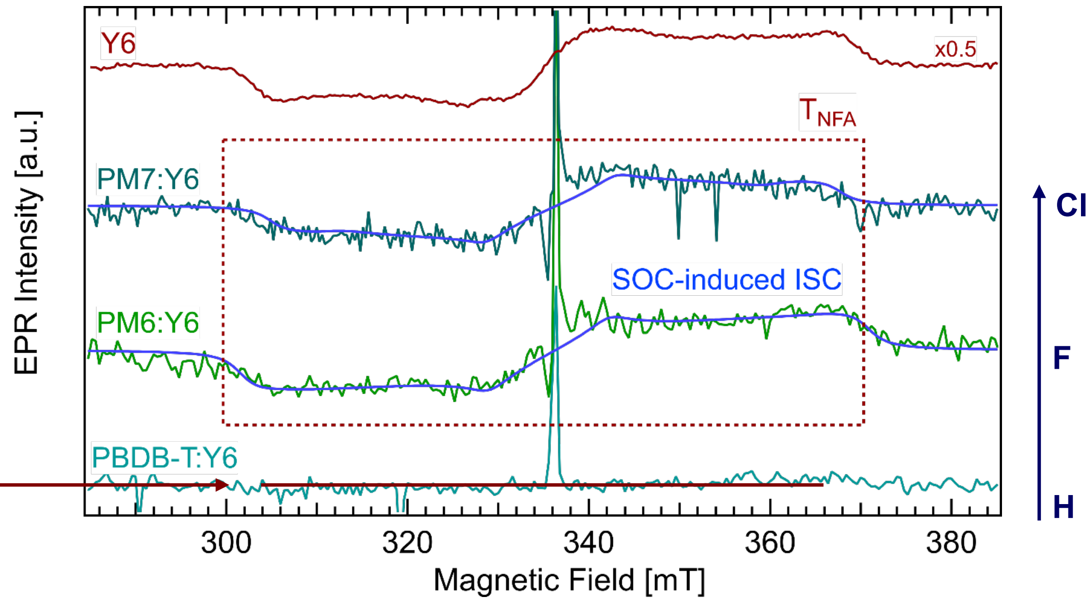
Triplet Excitons in OPV Blends



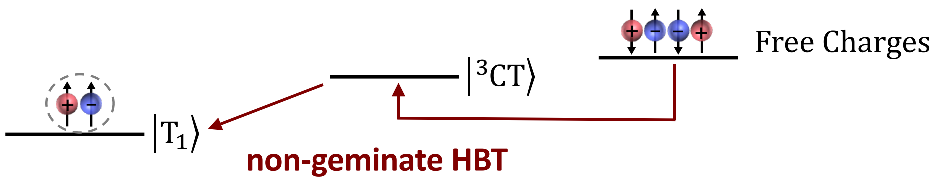
Triplet Excitons in PLDMR



Pathway by trEPR



→ PLDMR probes also **non-geminate HBT**

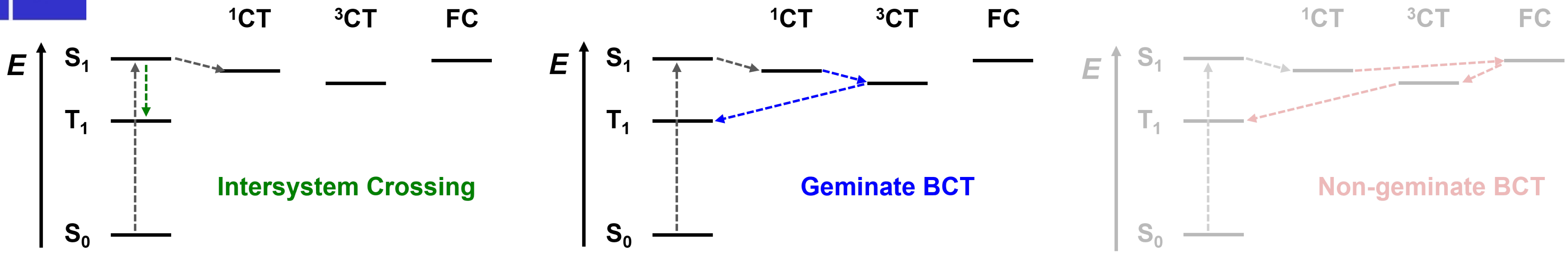


→ triplet excitons on Y6 by SOC-induced ISC

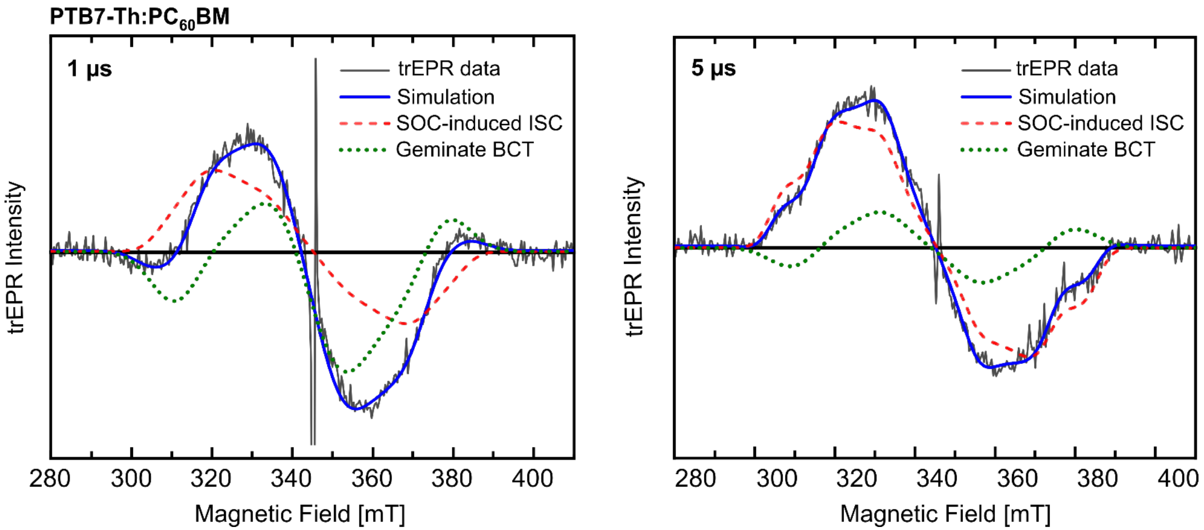
→ no Y6 triplets **by ISC** in PBDB-T:Y6

Adv. Funct. Mater. 2023
10.1002/adfm.202212640

Fullerene based OPV – trEPR



trEPR (A. Privitera, University Oxford, UK)



→ triplet exctions on donor

→ **SOC-induced ISC + geminate BCT**

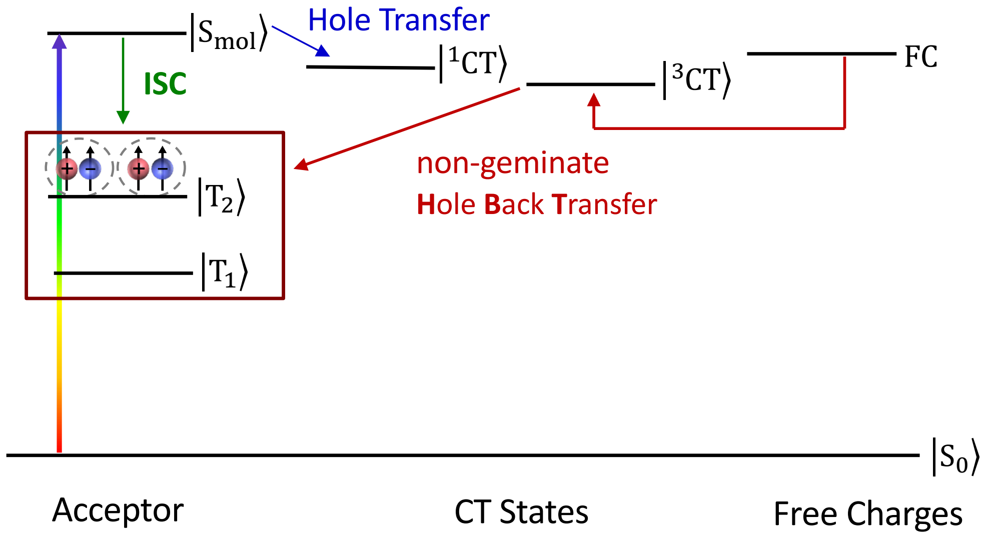
Summary: Triplet Excitons in OPV Blends

Triplet States

- Triplet excitons in all PM:Y-Series blends on NFA

Pathways

- SOC-induced ISC on NFA
  → to higher lying T_2 state (G. Londi, Y. Olivier)
  → higher ISC yield in PM6 and PM7 blends
- Non-geminate HBT in all studied PM:Y-Series blends
- Minor influence of halogenation of HBT rate



Efficiency-limiting pathways even in state-of-the-art combinations!

Toolbox for detecting Triplets
Adv. Energy Mater. 2022
10.1002/aenm.202103944

Halogenation and Triplets
Adv. Funct. Mater. 2023
10.1002/adfm.202212640

Triplet-Triplet Annihilation vs. Voc
arXiv: 2301.02112

Efficiency-Limiting Pathways in NFA-based Organic Solar Cell Blends – A Triplet Story

In collaboration with:

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University of Cambridge, UK

Giacomo Londi, Yoann Olivier, David Beljonne
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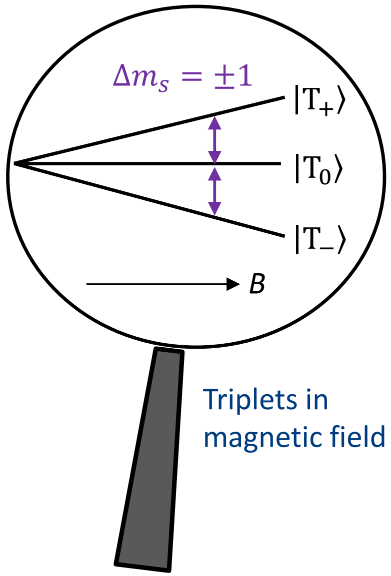

Triplets in magnetic field