

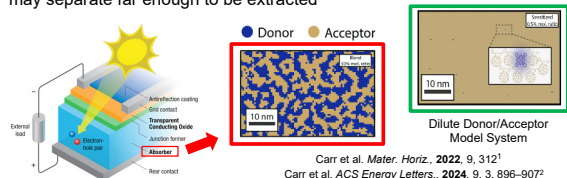
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Background

The active layer of the most efficient organic photovoltaic (OPV) devices is a blend of electron donors and acceptors that form a **bulk heterojunction**. After photoinduced electron transfer at an interface, electrons and holes may separate far enough to be extracted



Organic Solar Cell Device

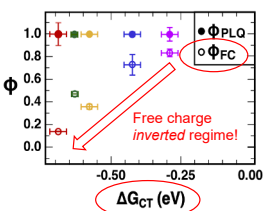
image from <https://www.nrel.gov/organic-photovoltaic-solar-cells.html>

How can we better understand charge transfer and separation in **model OPV systems** to better explain the efficiencies of OPV devices?

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

Marcus Rate Equation

Marcus Theory governs predictions of charge transfer in solution, can it explain charge transfer and separation in solid-state organics as well?



The **DRET Model**¹ predicts distance distributions of charge transfer where long-range (CS) and short-range (CT) transfer compete

Methods

Photoinduced Absorption Detected Magnetic Resonance (PADMR): RF/MW drives spin transitions of paramagnetic states formed under photoexcitation. This perturbs electronic dynamics and thus optical absorption

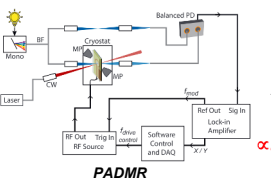
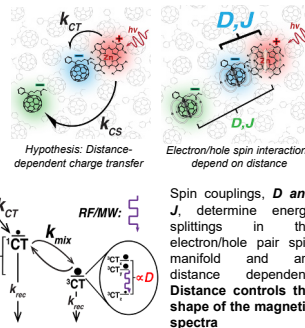


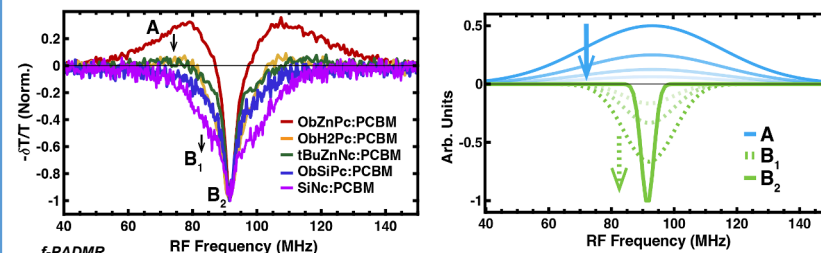
Image from Dill et al. *JPLC*. 2023. 14 (9), 2387-2394



Hypothesis: Distance-dependent charge transfer

Spin couplings, **D** and **J**, determine energy splittings in the electron/hole pair spin manifold and are distance dependent. Distance controls the shape of the magnetic spectra

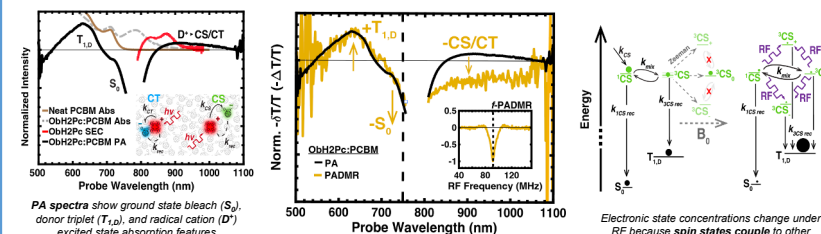
Results



f-PADMR
Different films, same conditions: 3.3 mT external magnetic field (B_0), 750 nm probe, 5-10 Kelvin

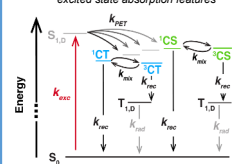
Arrows demonstrate the qualitative trend in the spectral shape with ΔG_{CT}

We observe a complex evolution of the shape of **f-PADMR** spectra that correlates with the changing driving force, ΔG_{CT}

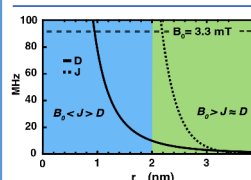


PA spectra show ground state bleach (S_0), donor triplet (T_{1D}), and radical cation (D^+) excited state absorption features

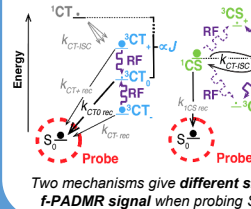
f-PADMR
Resonant RF/MW perturb steady-state electronic state concentrations, manifesting as changes in the PA spectra



Steady-state excitation distributes electronic state concentration into the excited states and ground state via charge transfer and recombination. We measure absorption features associated with those states in PA

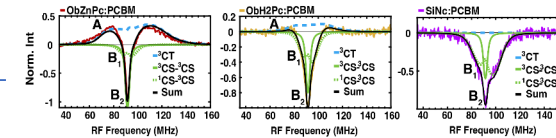


Two electron/hole pair spin coupling regimes
Blue: $J > D$
Green: $J < D$

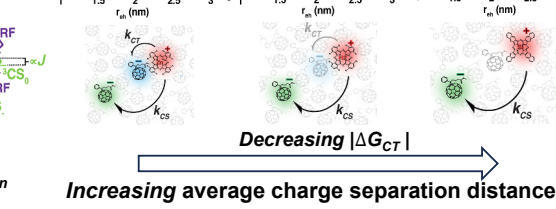
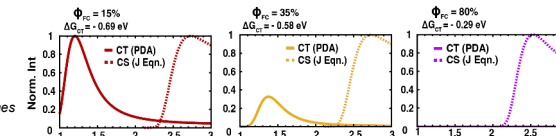


Two mechanisms give different sign **f-PADMR** signal when probing S_0

In PADMR, RF/MW frequencies resonant with **electron/hole pair spin transitions** drive **specific** changes in photoinduced absorption (PA) spectra that indicate spin-dependent recombination pathways

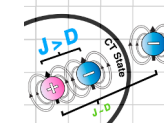


EasySpin¹ can model the spectra with spin pair distributions of defined J and D coupling. Corresponding distance distributions are calculated based on the fits



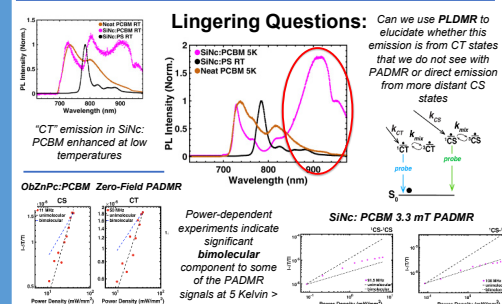
Decreasing $|\Delta G_{CT}|$
Increasing average charge separation distance

Conclusions & Future Work

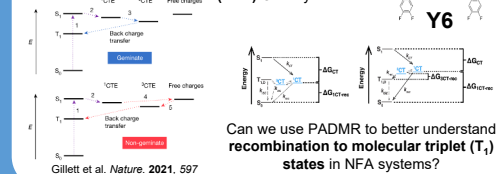


Charge transfer distance is controlled by the driving force, $|\Delta G_{CT}|$ in solid-state organic donor/acceptors. The most localized CT states are generated in measurable concentration only at large $|\Delta G_{CT}|$ beyond the free charge optimum

Suggests **the most localized CT states are predominantly a loss pathway in organic solar cells**



Can PADMR help us characterize charge dynamic in the "high-performance" non-fullerene acceptor (NFA) OPV systems?



Can we use PADMR to better understand recombination to molecular triplet (T_1) states in NFA systems?

References

- [1] Carr et al. *Materials Horizons*. 2022. 9, 312
- [2] Carr et al. *ACS Energy Letters*, 2024. 9, 3, 896–907
- [3] Dill et al. *The Journal of Physical Chemistry Letters*. 2023. 14 (9), 2387-2394
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Info & Acknowledgements

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