Observing Charge Separation Distance in Organic Donor-Acceptors with Photoinduced Absorption Detected Magnetic Resonance Spectroscopy

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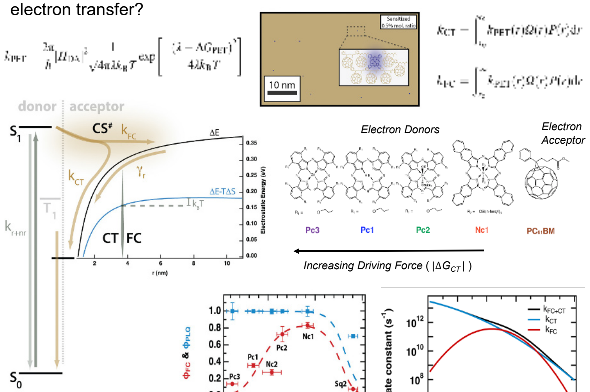
Motivation

How may we test a **distributed range electron transfer (DRET)**[1] model that explains free charge generation for organic donor-acceptor (D/A) systems using Marcus Theory and *distance-dependent* rates? What new spectroscopic tools can we use to test the model's prediction of there being a distribution of charge transfer (CT) state distances upon photoinduced electron transfer?



Images and data from Carr et al. Mater. Horiz., **2022**, 9, 312[1]

Methods

Photoinduced Absorption Detected Magnetic Resonance (PADMR) is a population-detected magnetic resonance (MR) technique that *correlates electronic transitions with MR transitions* by measuring changes in excited state absorption under modulated radiofrequency (RF) radiation resonant with electronic spin sublevel transitions. Our experimental design allows us to measure PADMR both at zero-field and in an applied magnetic field, allowing for extended versatility and easier interpretation.

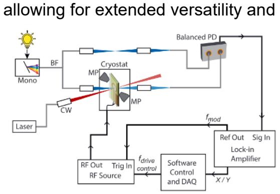
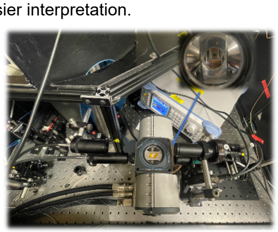
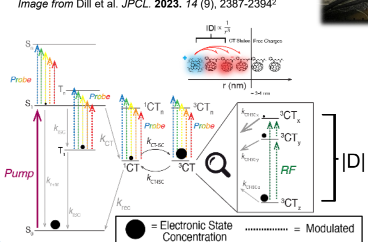


Image from Dill et al. JPCL. **2023.** *14* (9), 2387-2394[2]

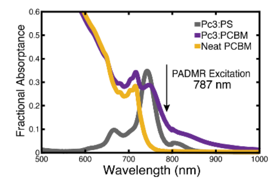


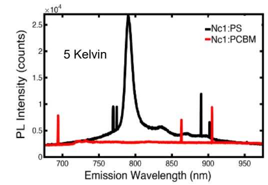


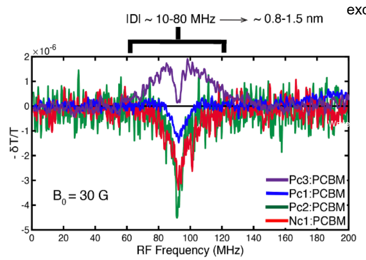
The energetic splitting of the spin sublevels of triplet states is due to **magnetic dipole-coupling, |D|**. We hypothesize that charge-pair distance can be approximated by |D| for charge-separated (CS) states with triplet character by measuring the RF frequency that drives transitions between triplet sublevels and perturbs electronic dynamics.

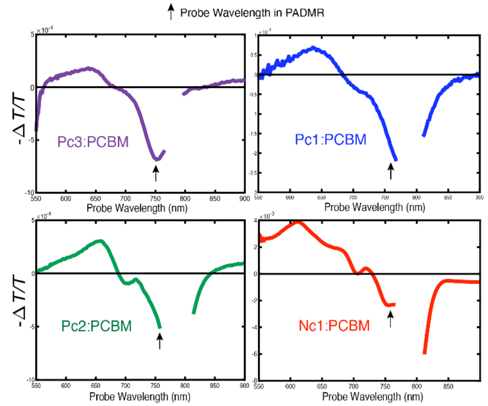
Results

Absorption data (below) show selective excitation of the electron donor in the dilute-D/A system and photoluminescence (PL) data show full quenching of donor's emission in the cryogenic conditions of PADMR

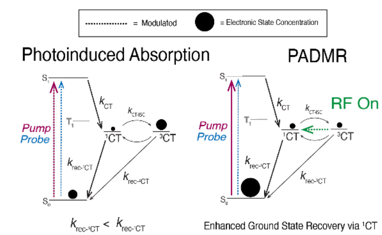




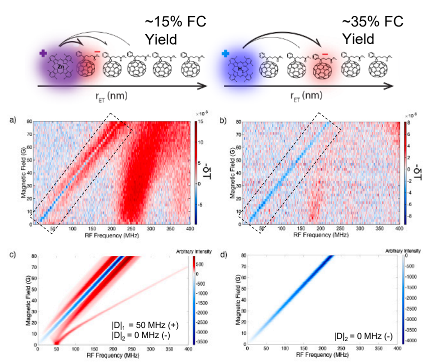


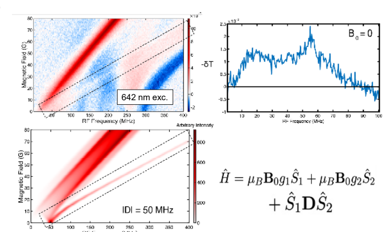


Photoinduced absorption (PA) spectra (above) show *electronic* state absorption under steady-state excitation conditions. For PADMR, the probe is set to the ground state (G.S.) and modulated RF is introduced. This allows us to measure MR effects on charge and/or exciton *recombination* dynamics.



Varying charge-pair distance with ΔG_{CT} is interpreted in PADMR. A *magnetic dipole-coupled* CS state with a G.S. recombination-*enhancing* MR effect is observed in Pc3:PCBM, whereas lower ΔG_{CT} systems show *only* an uncoupled CS state with a recombination-*depleting* MR effect of varying signal intensity. A proposed kinetic scheme for the Pc3:PCBM system shows a ¹CT state that may rapidly recombine to the G.S. or interconvert with slowly recombining ³CT states.



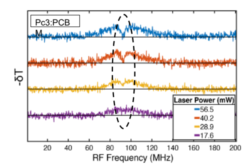


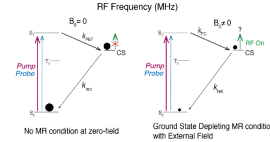
$$\hat{H} = \mu_B \mathbf{B}_0 g_1 \hat{S}_1 + \mu_B \mathbf{B}_0 g_2 \hat{S}_2 + \hat{S}_1 \mathbf{D} \hat{S}_2$$

"Bxf" PADMR spectra and comparison with EasySpin spectral simulation[3] of |D|-coupled radical pairs allow us to assign signals when moving from zero-field to an applied magnetic field (left). Qualitative differences are observed that indicate a CS state for Pc3:PCBM with a measurable |D| that is absent in the other systems (above)

Conclusions & Future Work

PADMR of a dilute D/A system with a large $|\Delta G_{CT}|$ and suppressed free charge yield measures a **CS state with an approximate separation distance of 0.8-1.5 nm** that is *not* measured in D/A systems with smaller $|\Delta G_{CT}|$ and higher free charge yields. This remains consistent with a model where free charges are generated from mostly long-range charge transfer controlled in part by $|\Delta G_{CT}|$, and tightly-bound CT states generated from short-range charge transfer.

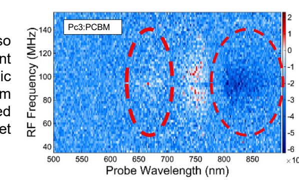




The negative PADMR CS signal is present only in an applied magnetic field and is narrower and more laser power dependent relative to the |D|-coupled species (left). This suggests that it arises from an MR transition for charges of *larger* inter-spin distance that recombine via an alternate mechanism, which will be further explored.

"*λxf*" PADMR (below) show what other electronic states are affected by the MR transitions. Both the |D|-coupled MR and narrower CS state MR have a depletive effect on an electronic state in the 800-875 nm region (associated with the radical cation of the donor), consistent with an MR transition *depleting* overall CS state concentration.

The MR transitions also appear to have different effects on electronic state in the 650-700 nm region, possibly associated with the molecular triplet state.



References

[1] Carr et al. *Materials Horizons*. **2022**, 9, 312
[2] Dill et al. *The Journal of Physical Chemistry Letters*. **2023.** *14* (9), 2387-239.4
[3] Stoll and Schweiger. *The Journal of Magnetic Resonance*. **2006**

Info & Acknowledgements

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