

UCR Initiative on Photovoltaics for Light, Energy, and Farming (UCR P-LEAF)

Lihua Xu (Libby), Bryan M. Wong

University of California Global Food Initiative Fellowship

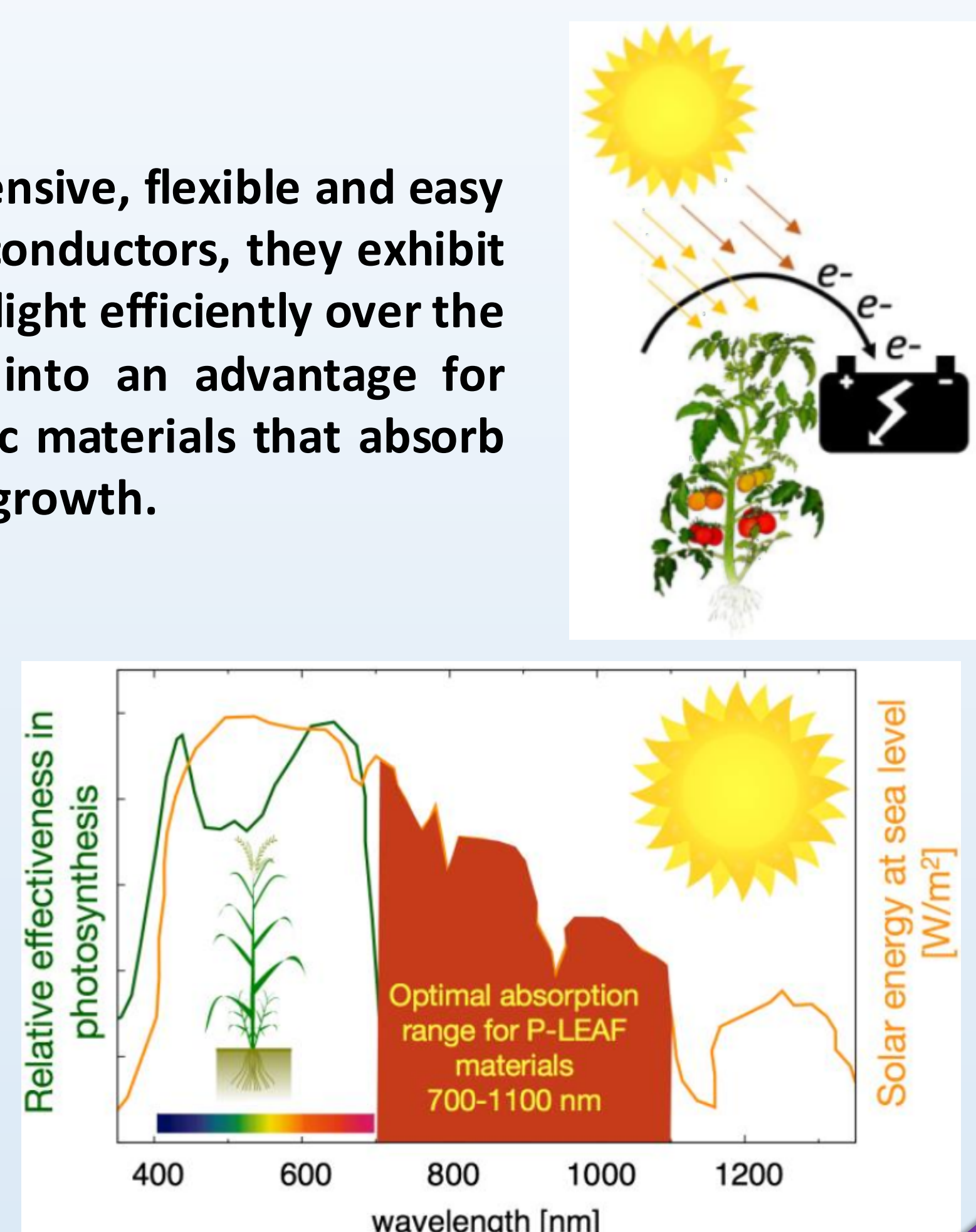
Introduction



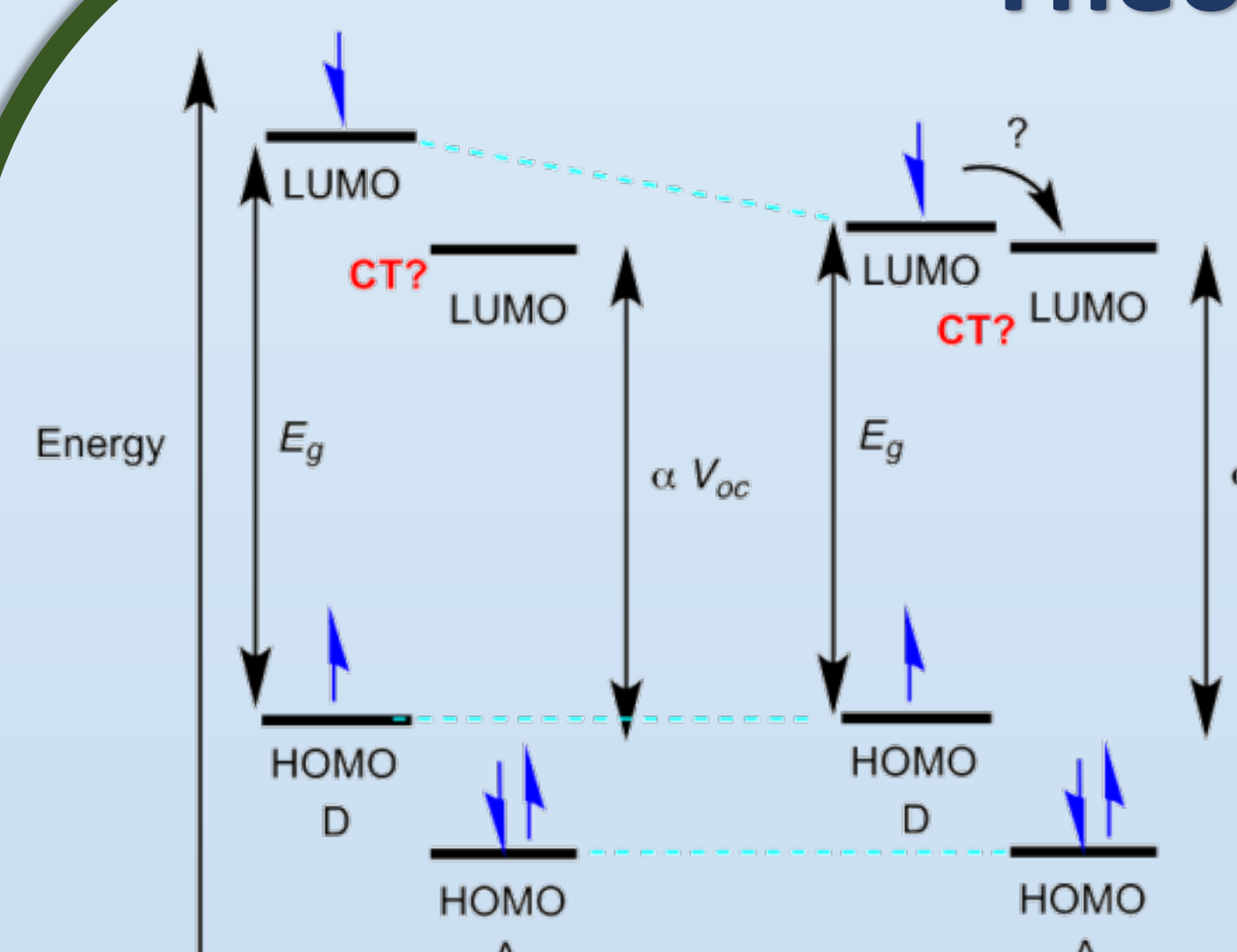
"The UCR Initiative on Photovoltaics for Light, Energy, And Farming (UCR P-LEAF)" aim to use computational methods to predict the first-generation organic-semiconducting materials specifically tailored for implementation as agricultural covers.

Though organic solar cells have the potential to be inexpensive, flexible and easy to manufacture compared with traditional inorganic semiconductors, they exhibit lower power conversion efficiencies as they do not absorb light efficiently over the entire solar spectrum. We plan to turn this limitation into an advantage for powering greenhouses by designing optoelectronic organic materials that absorb mainly at wavelengths outside the optimal range for plant growth.

We envision that solar cells made from such flexible and affordable materials could be used as covers or roofs of greenhouses in order to provide them with power, particularly when separated from the electrical supply grid. These energy-generating devices will be transparent to the shorter wavelengths of sunlight needed for plant growth and use the longer wavelengths for generating the power needed to heat, irrigate, or otherwise run the greenhouse, creating a zero-energy usage farming structure.



Theories & Methodologies



We will combine molecular or polymeric donor materials with a highly efficient fullerene-based electron acceptor, which absorbs minimal sunlight in the photosynthetic wavelength range of 400-700 nm.

In particular, we aim to tune the highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) energy levels of the donor material so that its optical energy gap (E_g) leaves a photosynthesis window, while maintaining a high open circuit voltage, V_{oc} . V_{oc} is proportional to the difference in the donor (D) HOMO energy and the acceptor (A) LUMO energy as in the figure.

To create optical organic materials for photovoltaics for energy and farming, we will lower E_g (the donor HOMO-LUMO gap) to absorb lower energy sunlight while maximizing V_{oc} (the donor HOMO-acceptor LUMO gap) to keep the power conversion efficiencies high for photo-induced electron transfer.

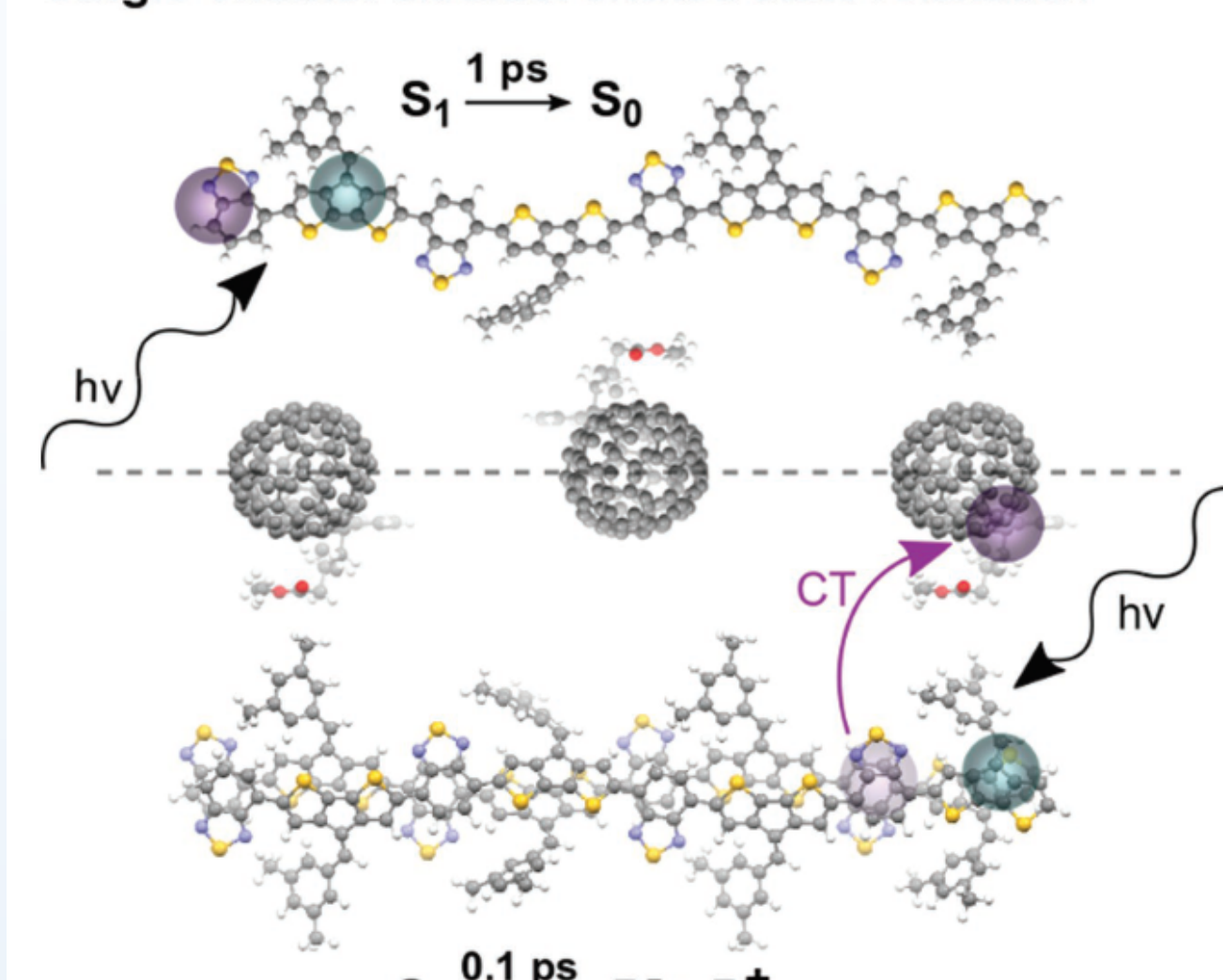
The power conversion efficiency of the cell is directly proportional to V_{oc} , the V_{oc} must be maximized while the E_g is tailored to absorb in the wavelength range 700-1000 nm. So that quantum computational approaches will be used: to engineer proper molecular orbital levels through examination of chemical structures and thereby avoid inefficient trial-and-error approaches.

Predictive modeling of material properties:

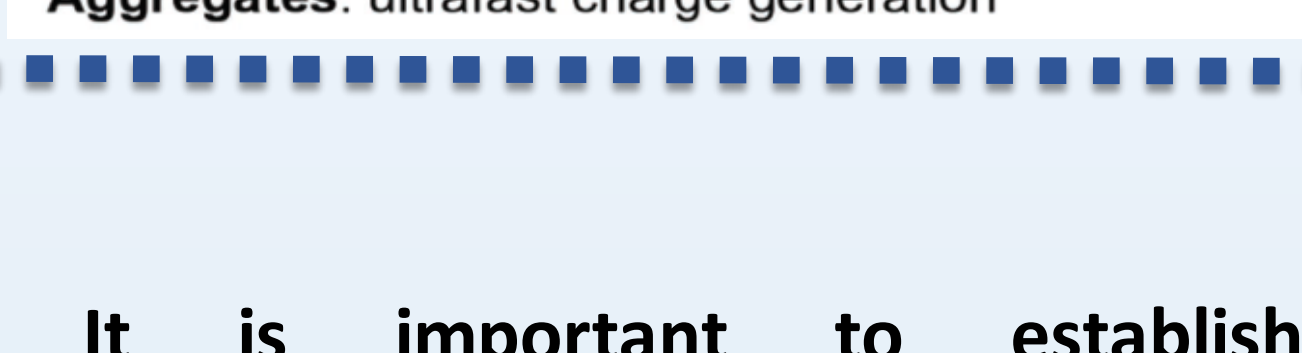
- Simulating photoexcitation and charge transfer for molecules in condensed phase environments;
- Explaining how substituents and their location on the donor molecules alter the absorption profiles, ionization potentials, electron affinity, and electron transfer energy;
- Screen desirable donor structures before attempting to synthesize new materials, reducing the synthetic efforts and costs;
- Identify charge transfer state that plays a key role in controlling V_{oc} by modeling the electronic coupling between the donor and acceptor as a function of the geometry of the donor-acceptor contact;

These series of theoretical calculations will support and guide the experimental efforts in designing new materials!

Single chains: ultrafast excited state relaxation



Aggregates: ultrafast charge generation



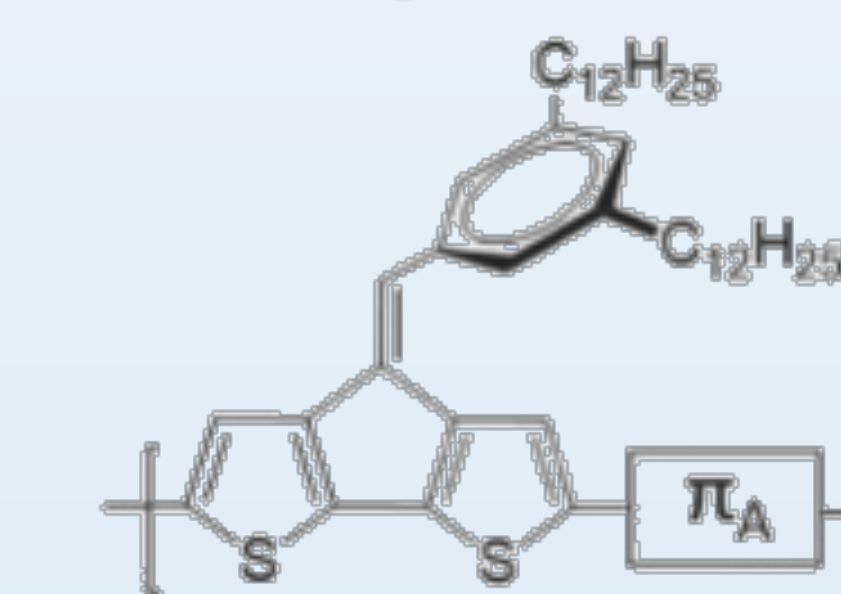
The Goal of This Study

- Establishing structure-function relationships that give rise to their emergent electronic properties.
- Characterize the extent to which processes in the solid-state such as excited state delocalization over aggregates or donor/acceptor charge transfer kinetically compete with intramolecular excitation relaxation.

Photophysical processes following excitation of electron (purple)-hole (teal) pairs by absorption of light energy ($h\nu$). Single polymer chains (top) exhibit ultrafast (≈ 1 ps) relaxation to the ground state (S_0) from singlet excitons (S_1), even in blended films with $PC_{71}BM$ acceptor molecules. Aggregates (bottom) show extended lifetimes in neat films and exhibit ultrafast polaron formation (P^{\pm} , ≈ 0.1 ps) in blended films via charge transfer with $PC_{71}BM$.

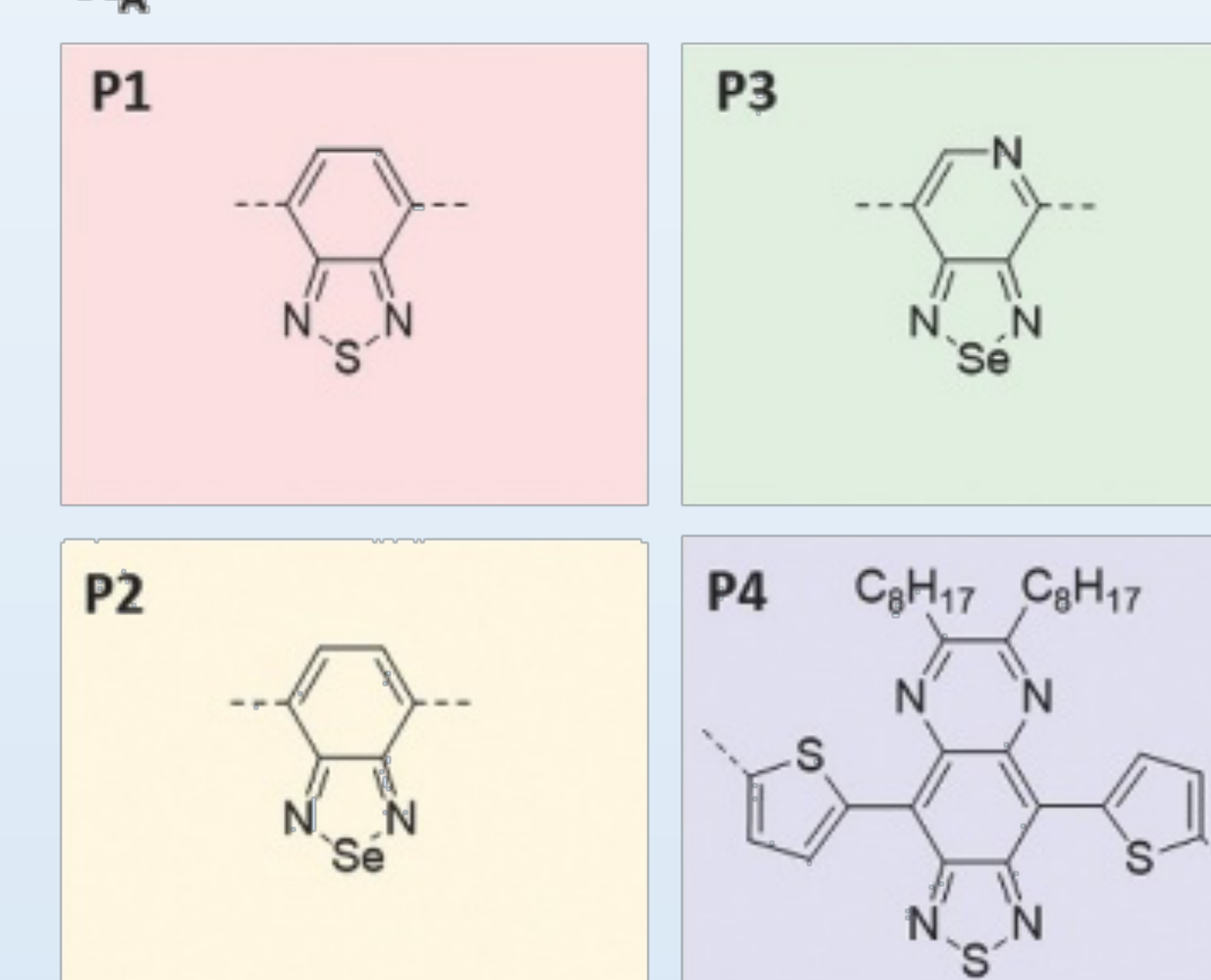
Materials Explored

It is important to establish structure-function relationships that give rise to the emergent electronic properties. Thus, it is informative to correlate native molecular energetics and relaxation dynamics with systematic chemical modification of the conjugated backbone.

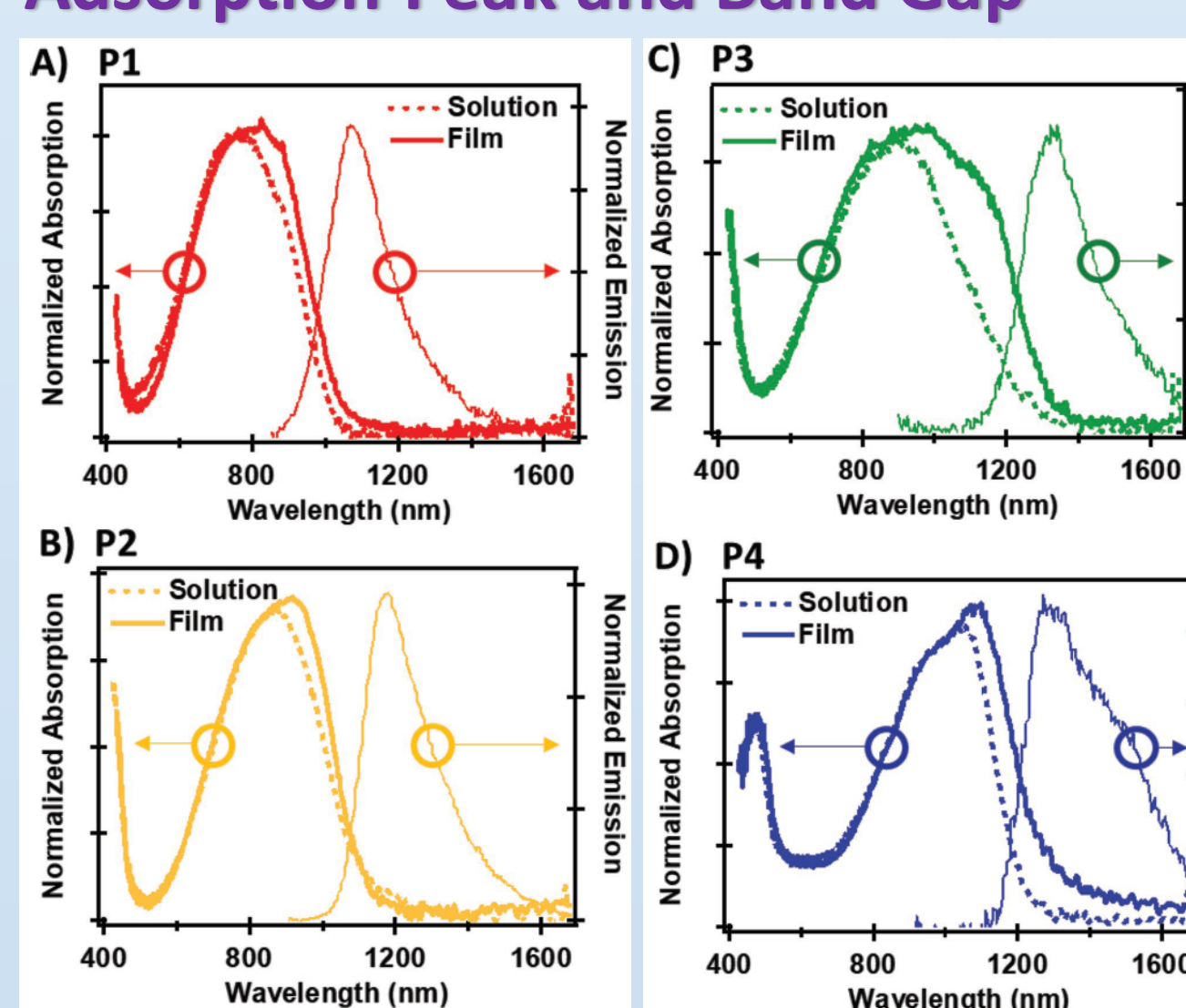


Molecular structures of the push-pull polymers used in this study. Where all polymers contain a exocyclic olefin substituted cyclopentadithiophene "push" unit, and the "pull" unit (π_A) varies as P1, P2, P3, and P4.

$\pi_A =$



Adsorption Peak and Band Gap



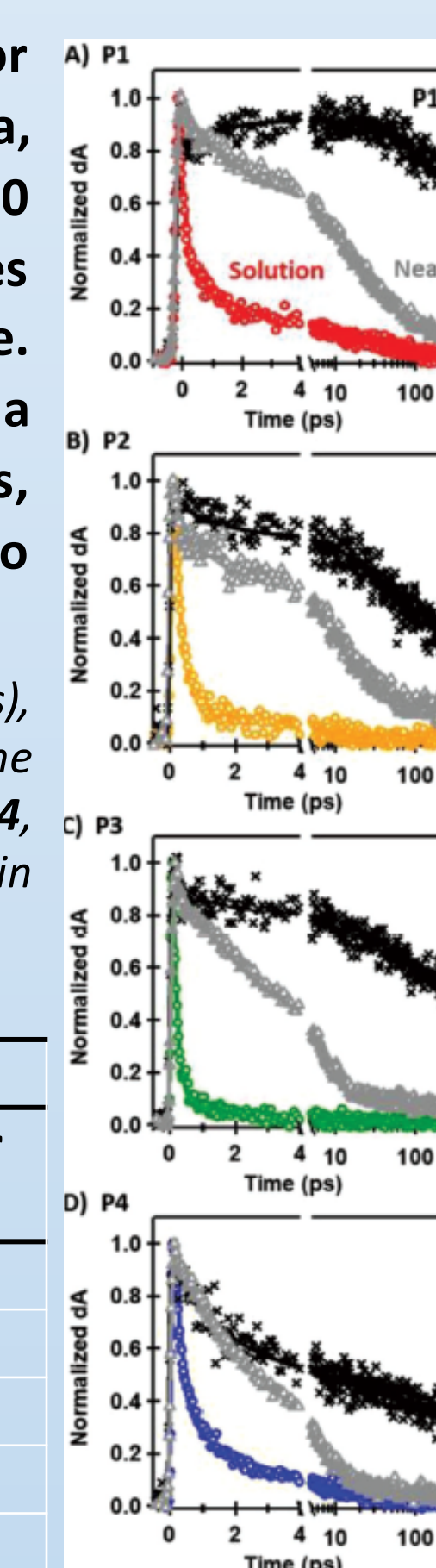
Results to Date

The polymer P4 contains the strongest acceptor unit and the lowest energy absorption maxima, with peaks in the solution phase at 960 and 1050 nm and an absorption onset of 0.98 eV. P4 includes flanking thiophene units in the polymer backbone. The lower optical gap of P4 is attributable to a higher HOMO energy. Using TD-DFT calculations, we find similar systematic shifts in absorption to lower energies for the P1-P4 series (Table).

Absorption and emission spectra for thin films (solid lines), along with absorption spectra for dilute chlorobenzene solutions (dotted lines) of a) P1, b) P2, c) P3, and d) P4, highlighting additional low-energy absorption peaks in thin films due to polymer aggregation.

Electronic Structure Calculations of P1-P4 Polymers

Excited State	P1		P2		P3		P4	
	Energy [eV]	Oscillator Strength	Energy [eV]	Oscillator Strength	Energy [eV]	Oscillator Strength	Energy [eV]	Oscillator Strength
1	1.3220	3.1408	1.2098	2.9381	1.0803	2.4219	0.8909	3.3065
2	1.5848	0.0159	1.4541	0.0010	1.3023	0.4248	1.0671	0.0077
3	1.7019	0.0244	1.5691	0.0422	1.4400	0.2370	1.1372	0.0061
4	1.7319	0.0399	1.5917	0.0022	1.4583	0.0128	1.2012	0.0083
5	1.8587	0.0177	1.7069	0.0085	1.4987	0.0180	1.3043	0.2089



Compared to the sub-picosecond lifetimes of single-chain excitations, we observe significantly slower exciton relaxation for polymer aggregates in thin films.

The P1-P3 films exhibit spectral evolution in the first picosecond that we attribute to decay of single-chain excitons, followed by decay on longer time scales of aggregate-based species with red-shifted bleach minima.

For P4 films, we observe only red-shifted aggregate spectra. The presence of both single-chain and aggregate-based excitons following photoexcitation of the P1-P3 films suggests that both types of excitons may be available for charge transfer with $PC_{71}BM$ in these blends, while P4 blends may be more heavily dominated by aggregate states. The extended lifetimes in thin films are likely due to increased electron-hole separation caused by singlet state delocalization over polymer aggregates.

Comparison of bleach decay in solutions (colored), neat films (gray), and PCBM blended films (black) for a) P1, b) P2, c) P3, and d) P4. Neat film and polymer: $PC_{71}BM$ data are collected at $2-4 \times 10^{17}$ absorbed photons cm^{-2} at pump wavelengths of 620 nm for P1, 730 nm for P2, and 920 nm for P3-P4.

Conclusions

- We show that polymer aggregation plays a key role in ultrafast carrier formation while avoiding limitations from quickly decaying excitons in these infrared-absorbing materials.
- The results have important implications for the further development of organic infrared optoelectronic devices, which can be used as light harvesting materials.

Publications:

Preferential Charge Generation at Aggregate Sites in Narrow Band Gap Infrared Photo-responsive Polymer Semiconductors
Advanced Optical Materials, 6, 1701138 (2018)

Acknowledgements

Dana B. Sulas
Alexander E. London
Lifeng Huang
Zhenghui Wu
Tse Nga Ng
Cody W. Schlenker
Jason D. Azoulay
Matthew Y. Sfeir

