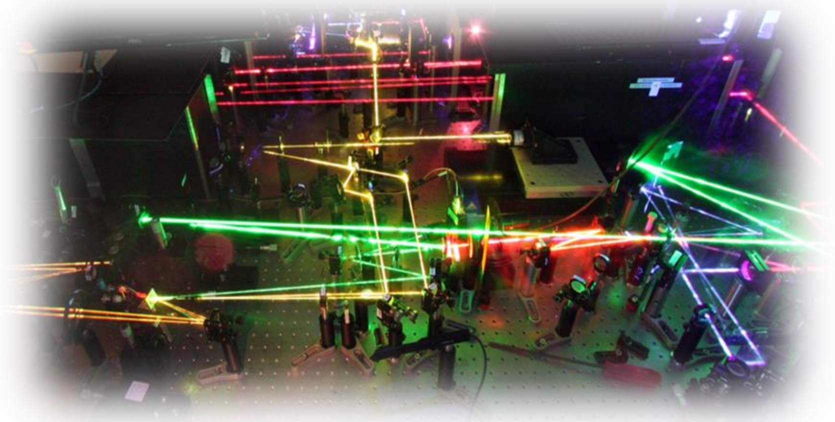

Embrace the darkness

From singlet fission to exciton-polaritons

Andrew J Musser
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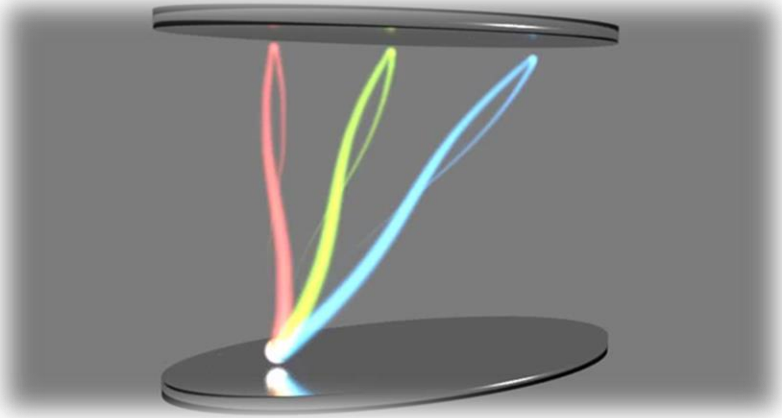

Light-Matters Group @ Cornell C&CB

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Ryan Pinard
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Sean Griffin, MSE
Pedro Oliveira, Phys
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Trevor Geraghty (BS, OSU)
Aaron Li (BS, MIT)
Nicole Silver (BS, CU Boulder)
Stavrini Tsangari (BS, Arizona/Ultima Genomics)

Air Force Office of Scientific Research
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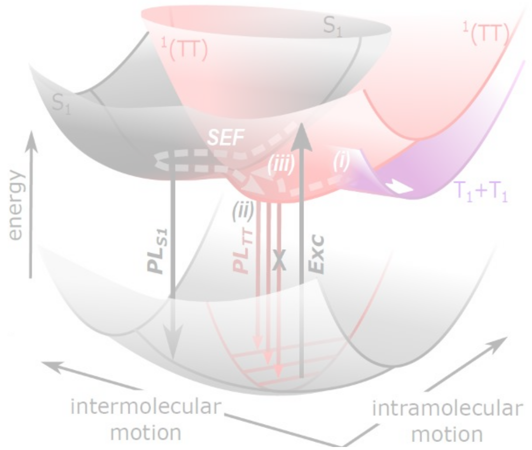
Cornell University
Cornell Atkinson Center for Sustainability
The College of Arts&Sciences
Alfred P. Sloan Foundation
U.S. Department of Energy Office of Science
Condensed Phase and Interfacial Molecular Science (CPIMS)
Chemical Sciences, Biosciences, and Geosciences Division
NSF



Singlet fission:

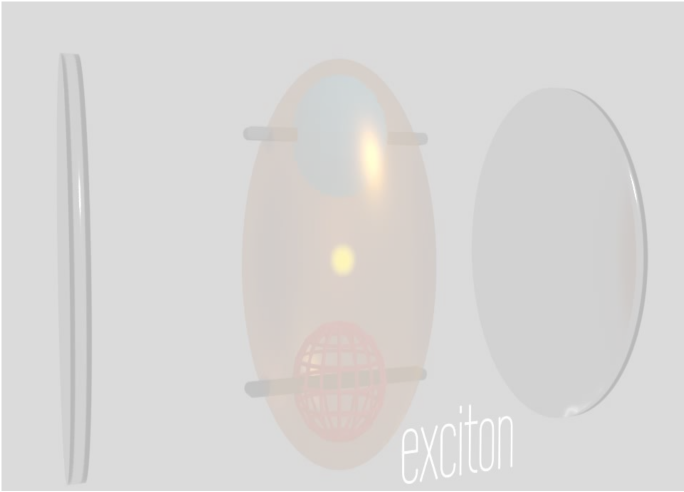
mechanism & design?

Fallon *JACS* **2019**
Pandya *Chem* **2020**
Bossanyi *Nat Chem* **2021**
Maity, Kim *Nat Commun* **2022**
Majumdar, Mukherjee *JACS* **2023**
Kim, Bain *under review*
Majumdar, Mukherjee *in preparation*
Mukherjee *in preparation*

Exciton polaritons:

redirecting molecular photochemistry

Polak *Chem Sci* **2020**
Renken *J Chem Phys* **2021**
Pandya *Nat Commun* **2021**
Pandya *Adv Sci* **2022**
Khazanov *Chem Phys Rev* **2023**
Kim *ACS Nano* **2023**
George *under review*
Gunasekaran *under review*
Mukherjee *in preparation*



Light-Matters @ Cornell C&CB

Vibronic dynamics:

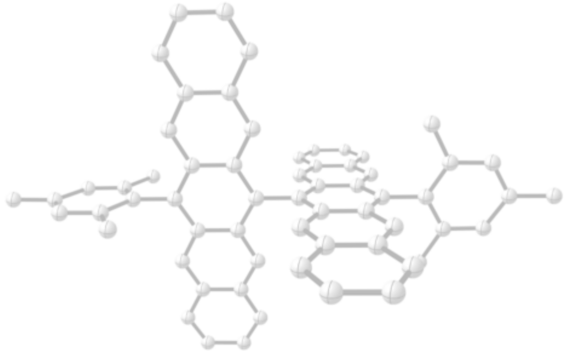
to inspire molecular design?

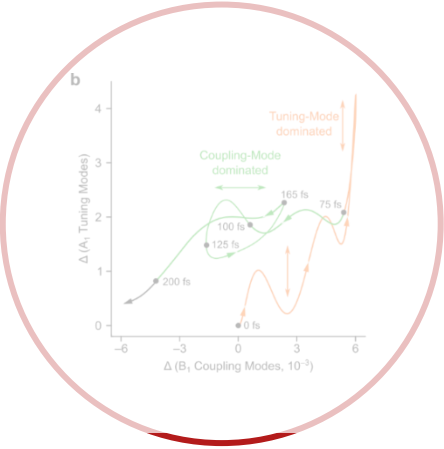
Schnedermann *Nat Commun* **2019**
Alvertis *JACS* **2019**
Kim *Adv Phys X* **2021**
Bain, *in preparation*
Khazanov, *in preparation*

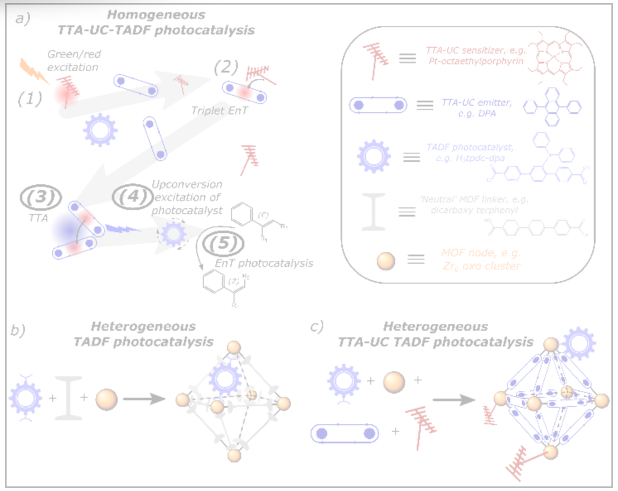
Photocatalysis:

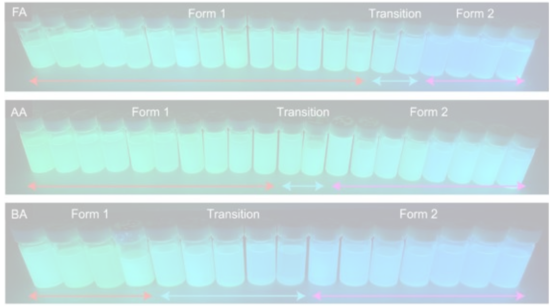
Mechanisms & enhancing function in crystalline frameworks

Halder, Bain, *JACS* **2023**
Xu, Vonder Haar *ChemComm* **2023**
Halder, Bain *Chem Mater* **2023**
Qiao *Nature Catalysis* **2023**
Vonder Haar *in preparation*

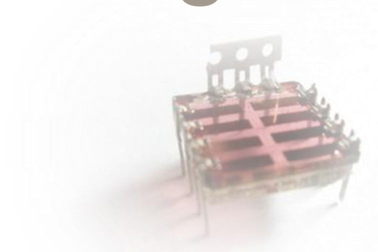


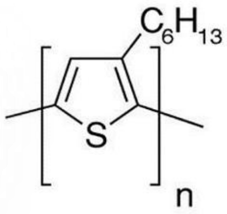


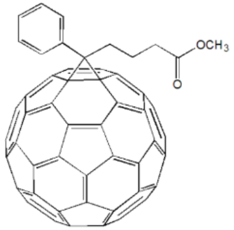




Organic semiconductors for fun & profit

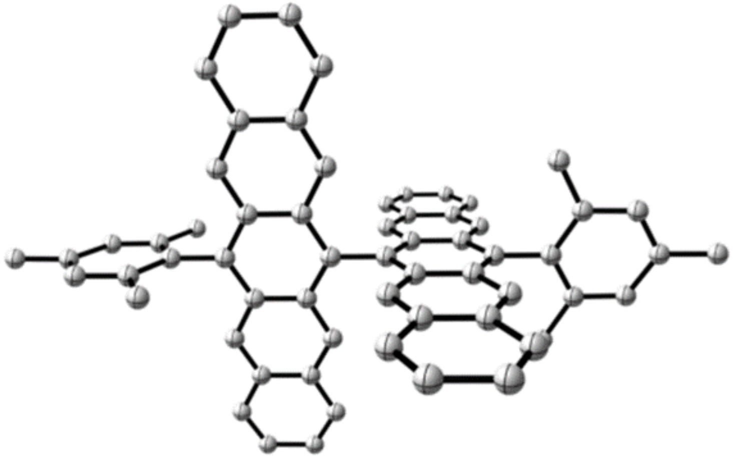


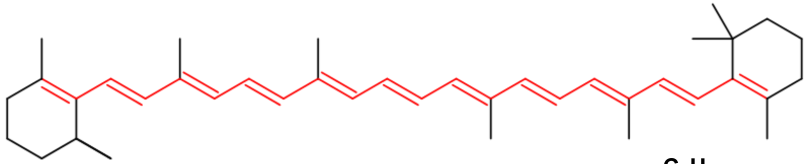


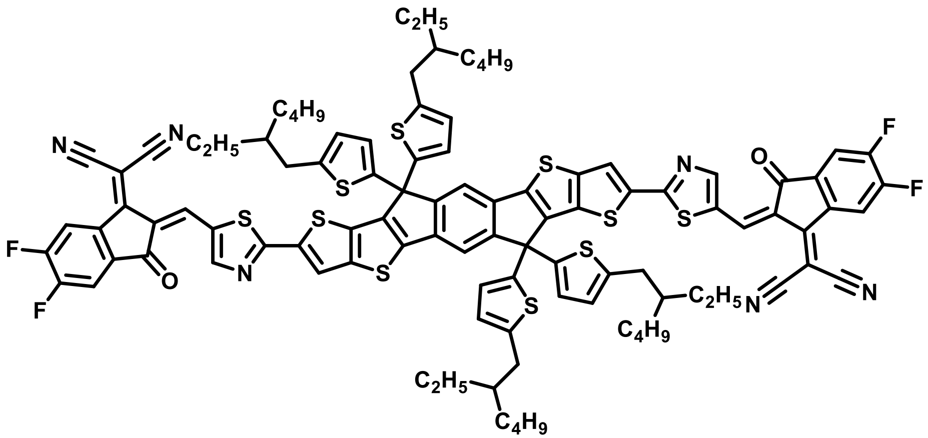


- Cheap & cheerful!
- Easy processing!
- Endless versatility!

- But…

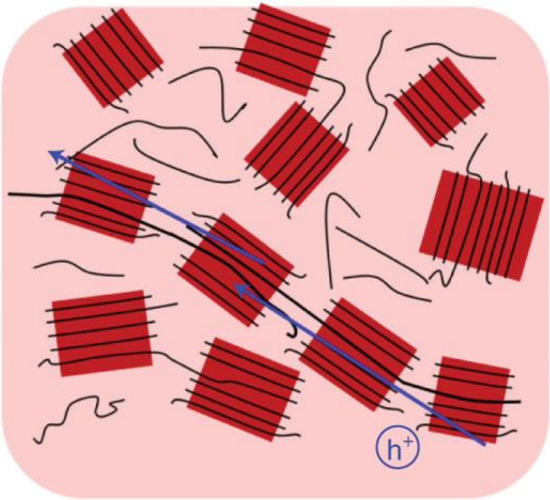


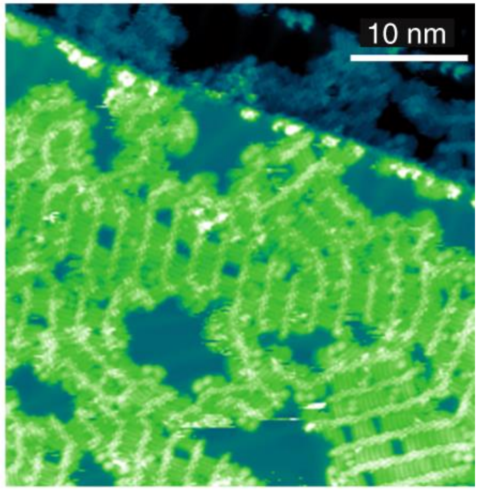




Packing problems

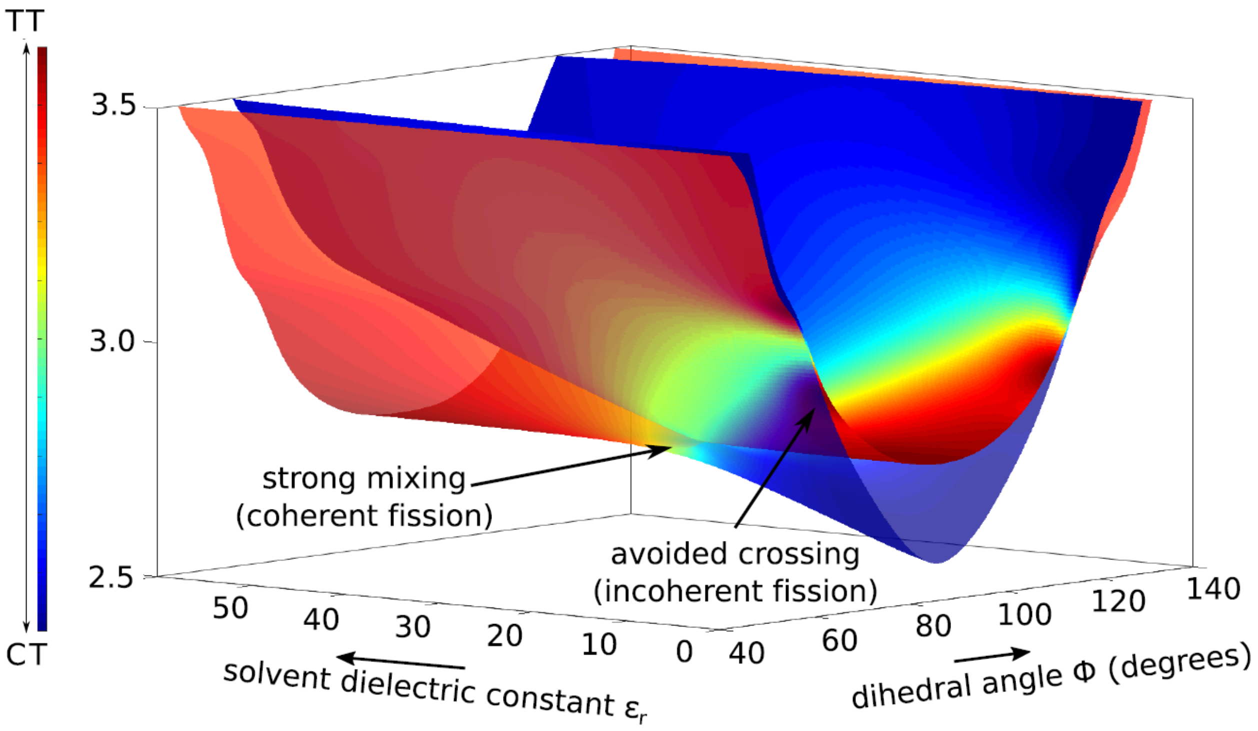
- Strongly localized Frenkel excitons
- Intermolecular couplings govern transport & photophysics
- Low-temp soft materials → defects & grain boundaries dominate!

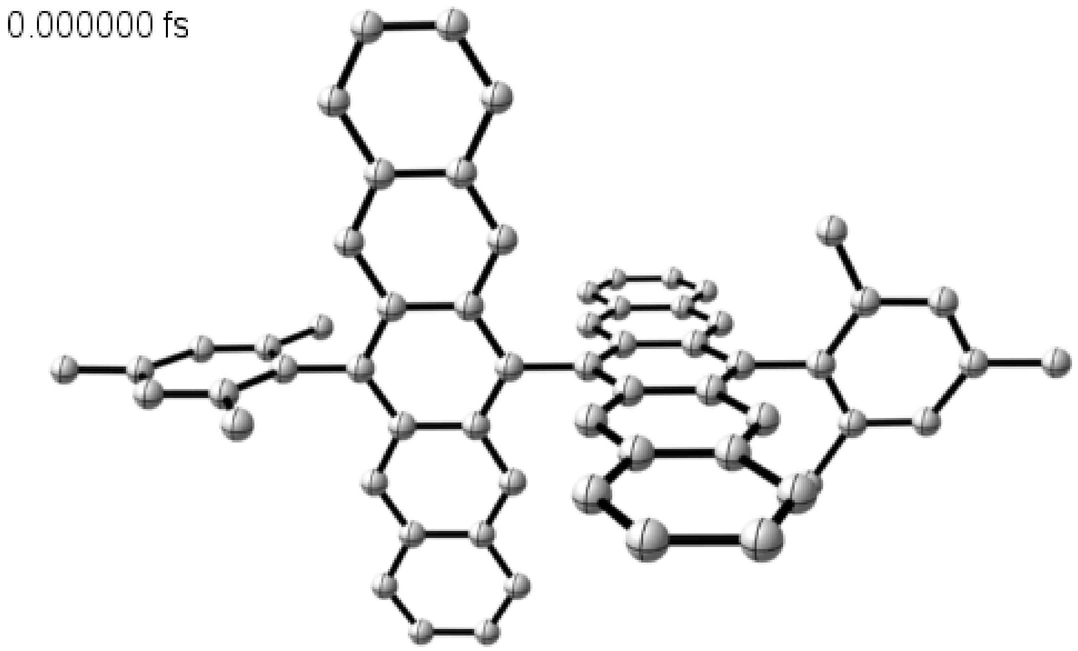




Fratini et al., *Nature Materials* 2020

Electron-phonon coupling





- Transitions dressed by vibronic coupling
- Vibrations (thermal & optically induced) cause disorder & carrier localization

→ drive electronic transitions

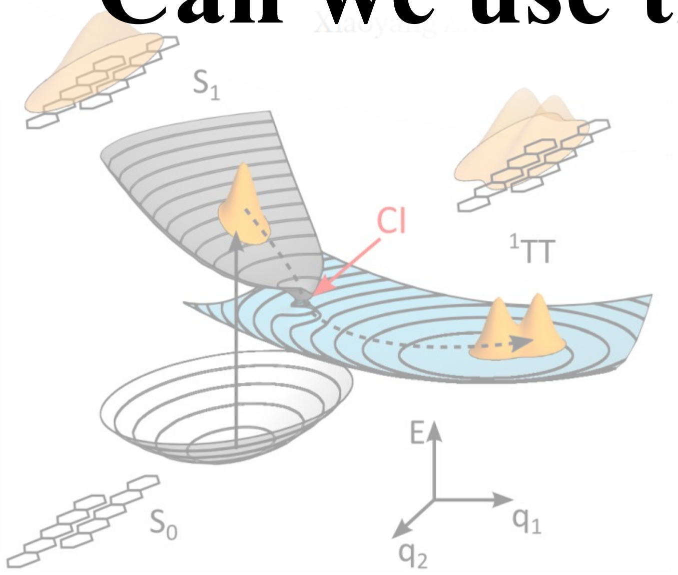
→ mix states of different character

Musser et al., Nature Physics 2015
Stern et al., Nature Chemistry 2017
Schnedermann… Musser, Nature Communications 2019
Musser & Clark, Annu Rev Phys Chem 2019
Alvertis… Musser, J Am Chem Soc 2019
Kim & Musser, Advances in Physics: X 2021
Bossanyi et al., Nature Chemistry 2021

Vibronic coherence & mixing are ubiquitous

REVIEW
doi:10.1038/nature21425

But does it matter, or does it 'just happen'?
Can we use this complexity to our advantage?

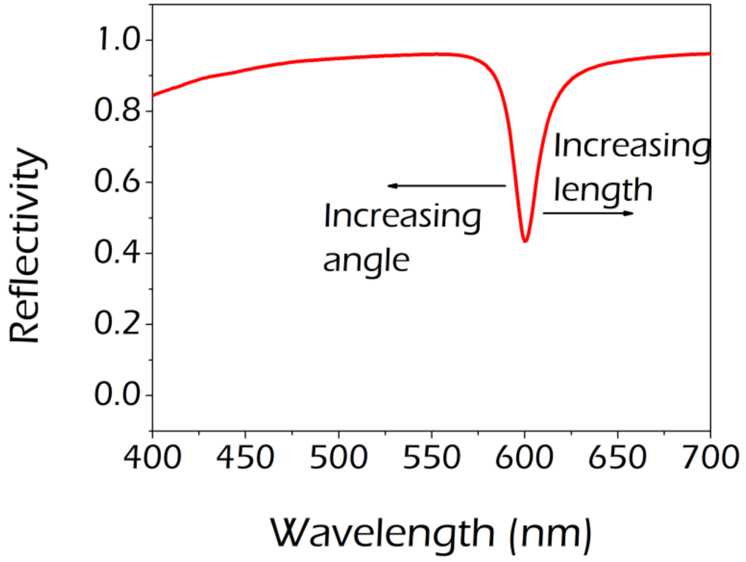


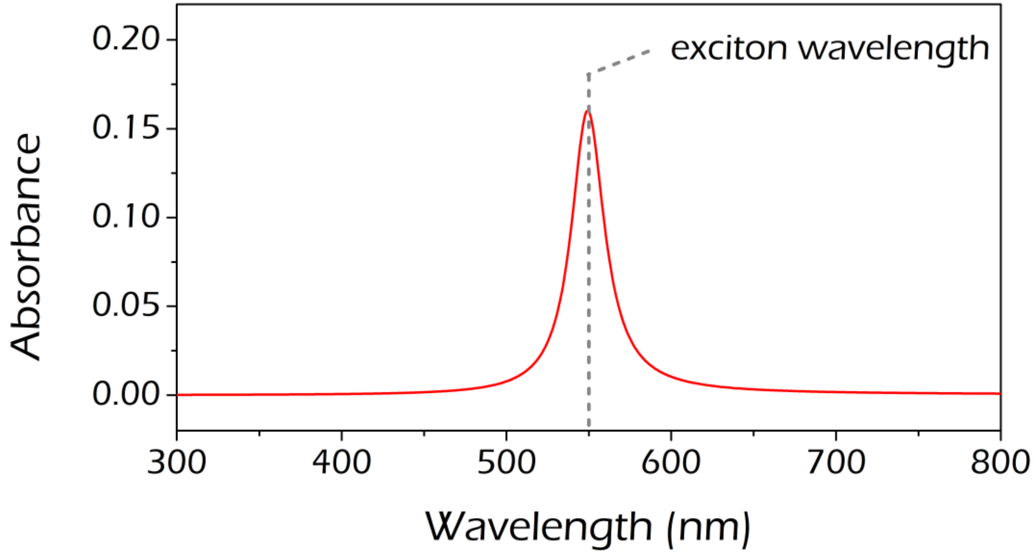
CHEMICAL REVIEWS
Review
Cite This: Chem. Rev. 2018, 118, 6975–7025
pubs.acs.org/CR

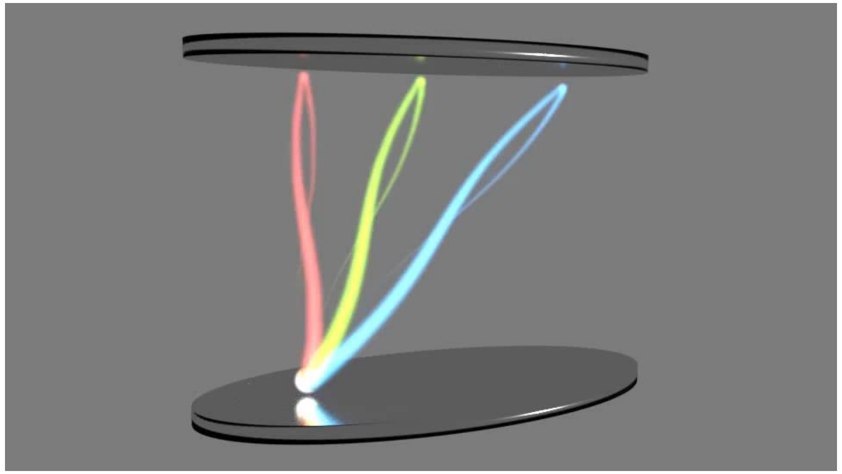
Spin-Vibronic Mechanism for Intersystem Crossing

Thomas J. Penfold,[*,†] Etienne Gindensperger,[‡] Chantal Daniel,[‡] and Christel M. Marian[§]

Strong light-matter coupling

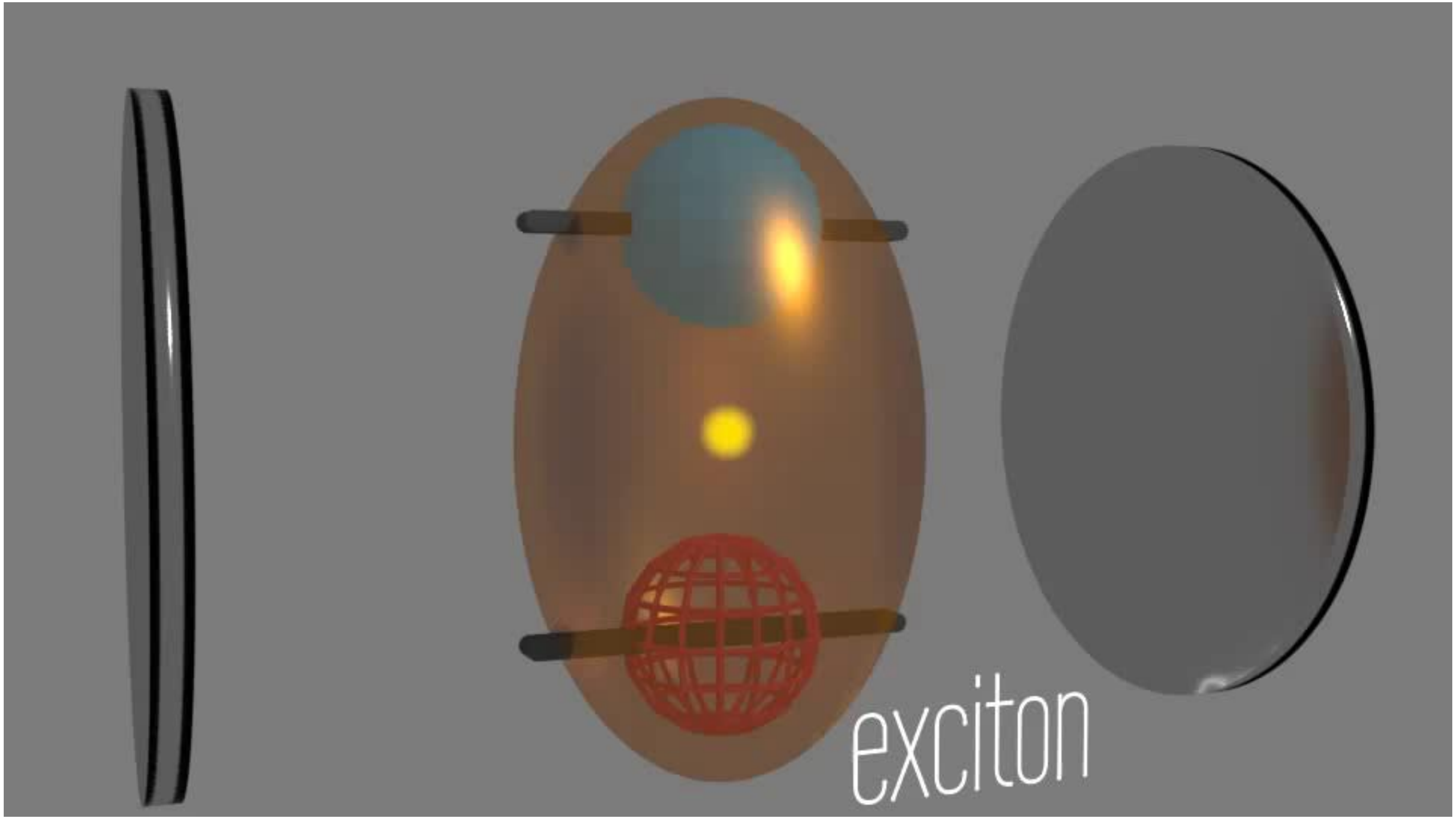






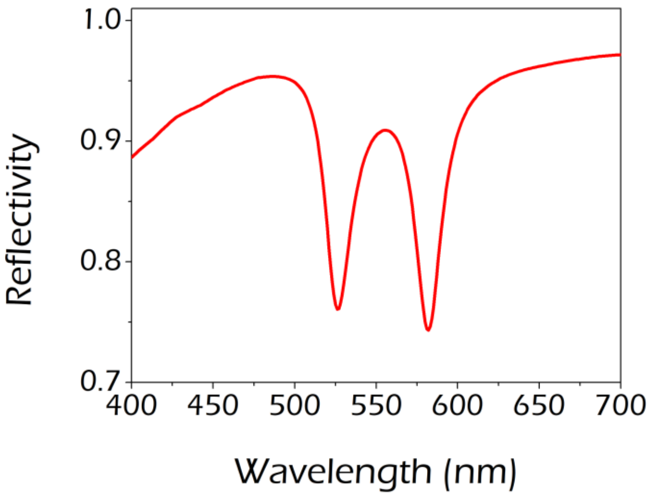
- Light: confined photon modes between closely spaced mirrors
- Matter: semiconductor exciton transition

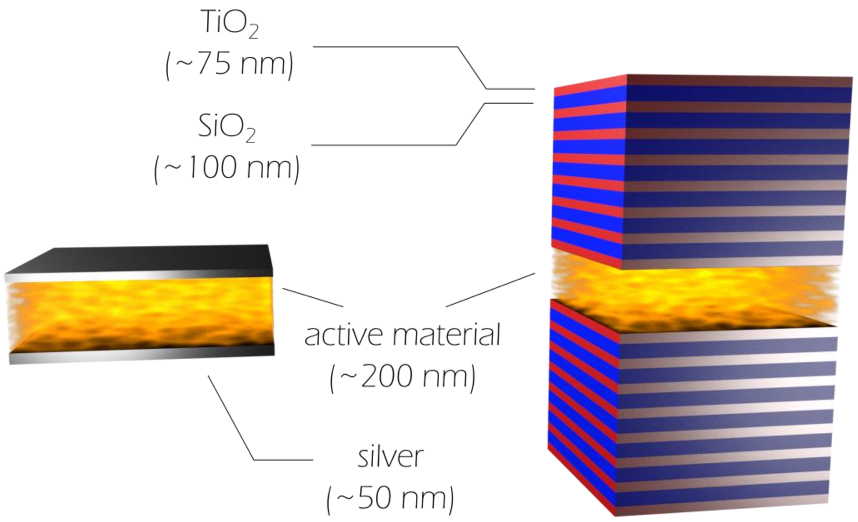
‘Polariton’ formation

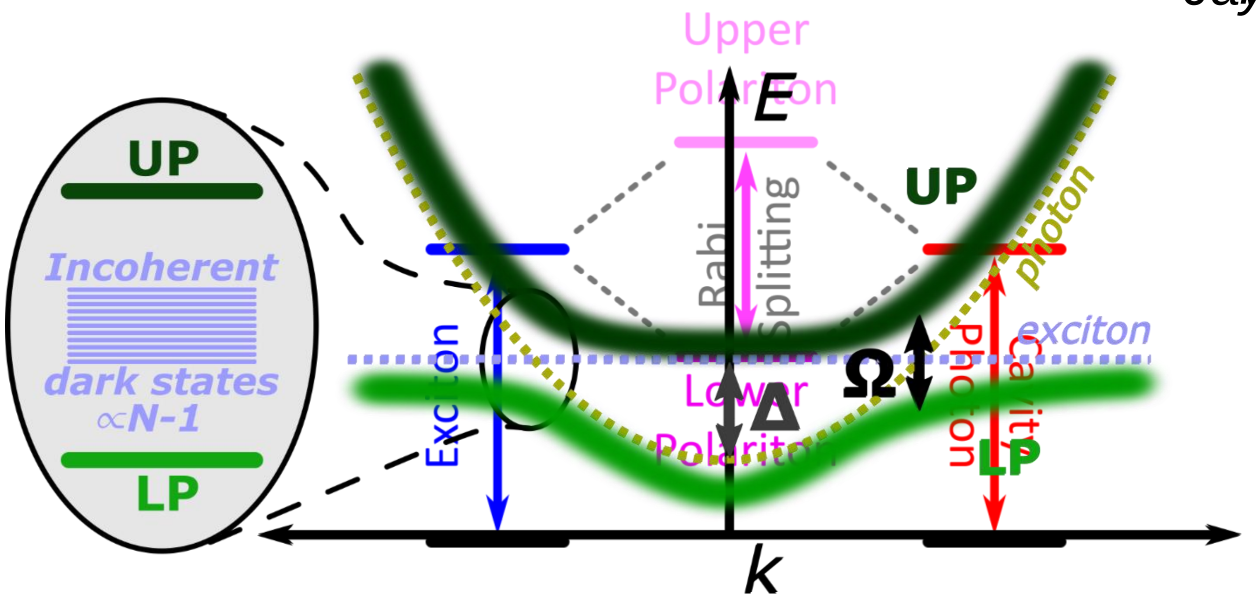


Video Credit: Dr. Dave Coles

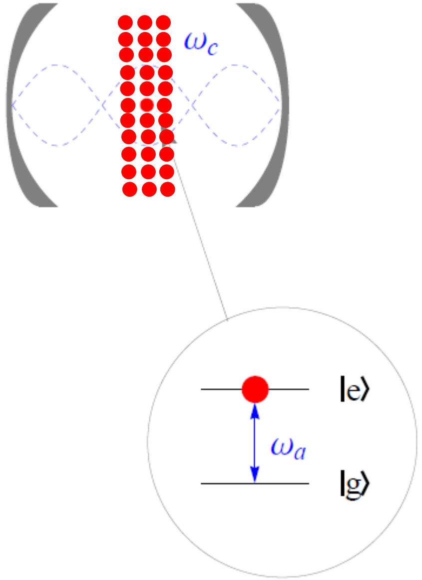
‘Polariton’ formation







Jaynes-Cummings / *Tavis-Cummings*



Light-matter interaction forms hybrid states at new energies with new properties

Unexpected effects in organic polaritons
^ and often inexplicable

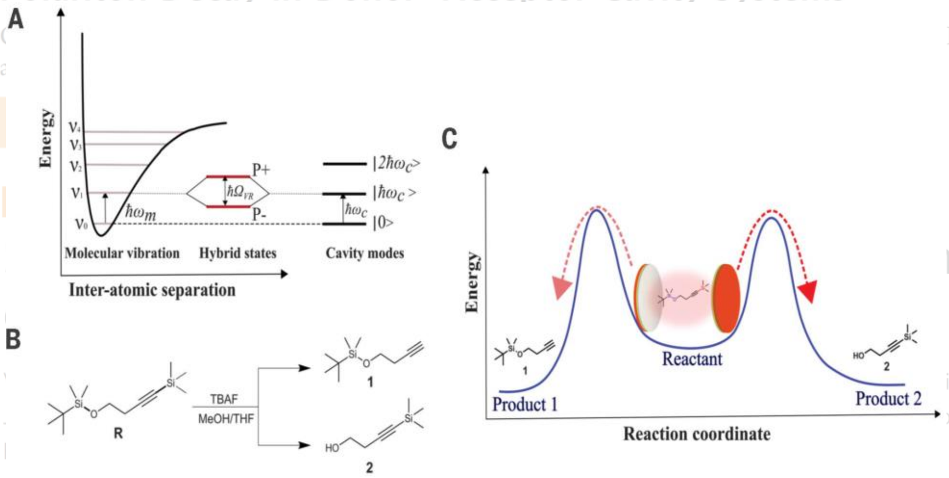
ARTICLES
PUBLISHED ONLINE
nature materials

CHEMISTRY

Tilting a ground-state reactivity landscape by vibrational strong coupling

A. Thomas[1]*, L. Lethuillier-Karl[1]*, K. Nagarajan[1], R. M. A. Vergauwe[1], J. George[1]†, T. Chervy[1]‡, A. Shalabney[2], E. Devaux[1], C. Genet[1], J. Moran[1]§, T. W. Ebbesen[1]§

Polariton Decay in Donor–Acceptor Cavity Systems



nature
ARTICLES

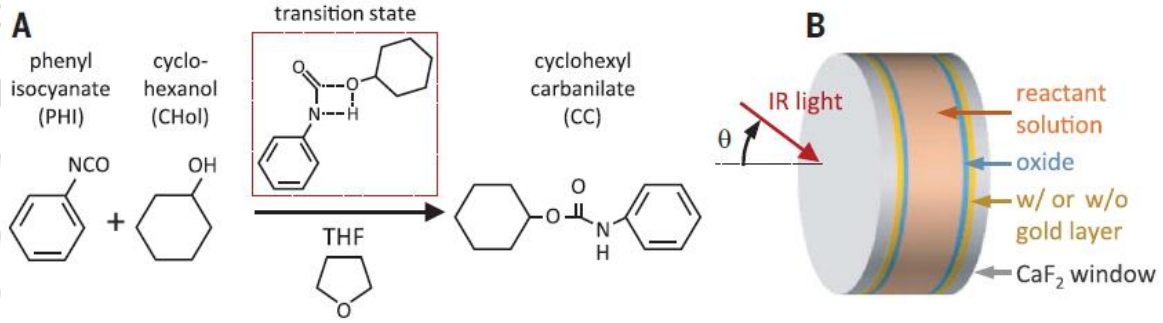
CHEMISTRY

Modification of ground-state chemical reactivity via light–matter coherence in infrared cavities

Wonmi Ahn[1], Johan F. Triana[2], Felipe Recabal[2], Felipe Herrera[2,3]*, Blake S. Simpkins[4]*

J. Schachenmayer[4], C. Genes[5], G. Pupillo[1,2], P. Samorì[1] and T. W. Ebbesen[1]*

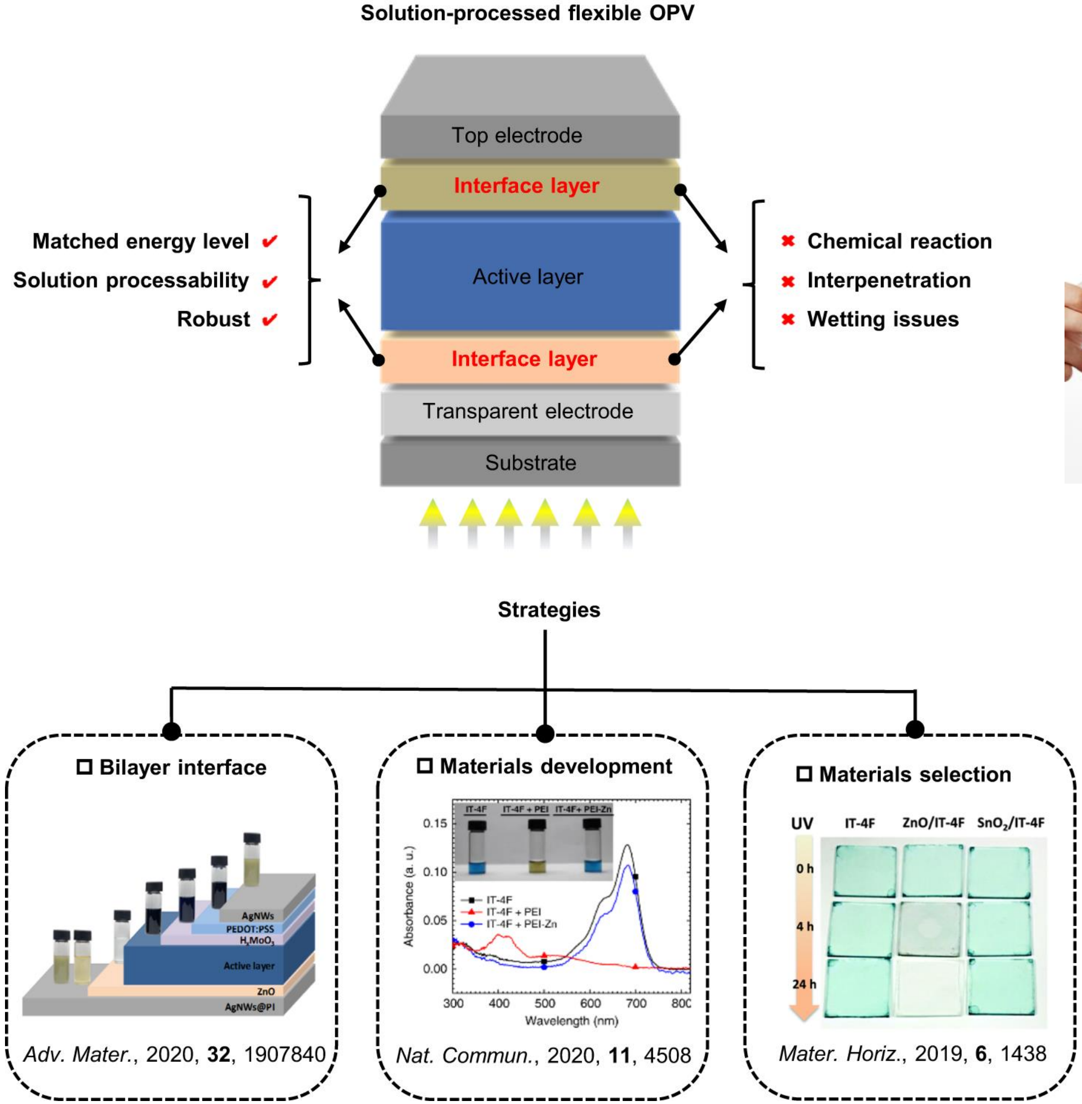
https://doi.org/10.1038/s41467-021-22183-3 OPEN



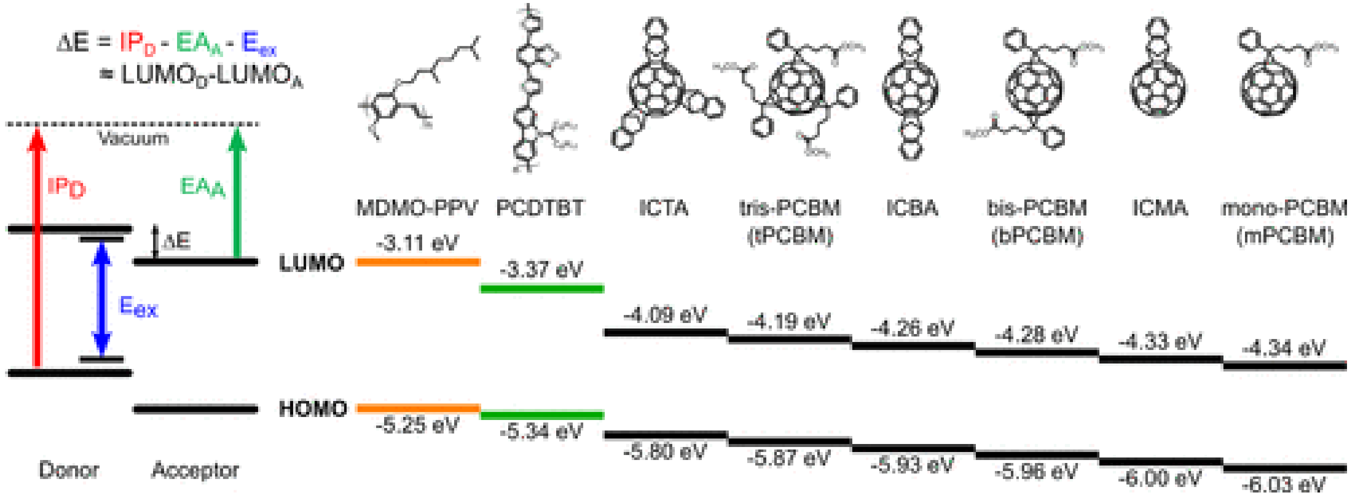
Tuning the Work-Function Via Strong Coupling

James A. Hutchison, Andrea Liscio, Tal Schwartz, Antoine Canaguier-Durand, Cyriaque Genet, Vincenzo Palermo, Paolo Samorì, and Thomas W. Ebbesen*

Inspired by organic electronics



Sun et al., npj Flex Elec 2022

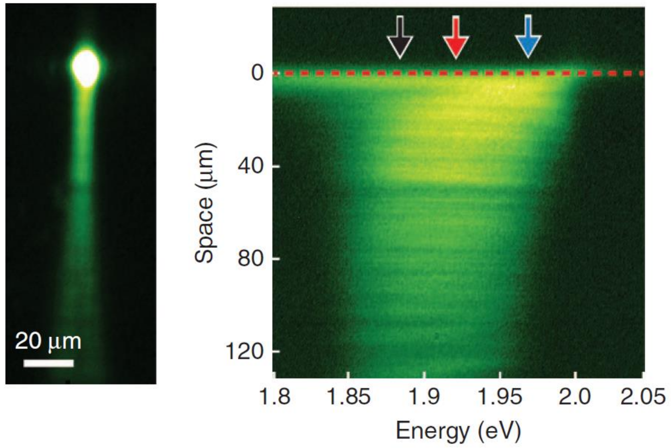


Jakowetz et al., JACS 2016

Polariton-mediated energy transport

- Interlayer donor-acceptor transfer well beyond FRET radius

- Intralayer energy transport over 10's μm



Sanvitto, *Light: Sci & App* 2017

- Rates and states unknown!
- And can we control it?

ARTICLES
PUBLISHED ONLINE: 4 MAY 2014 | DOI: 10.1038/NMAT3950
nature materials

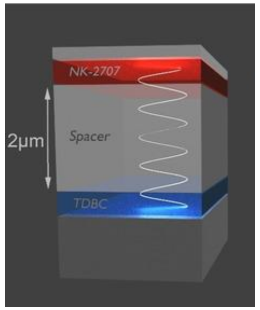
Polariton-mediated energy transfer between organic dyes in a strongly coupled optical microcavity

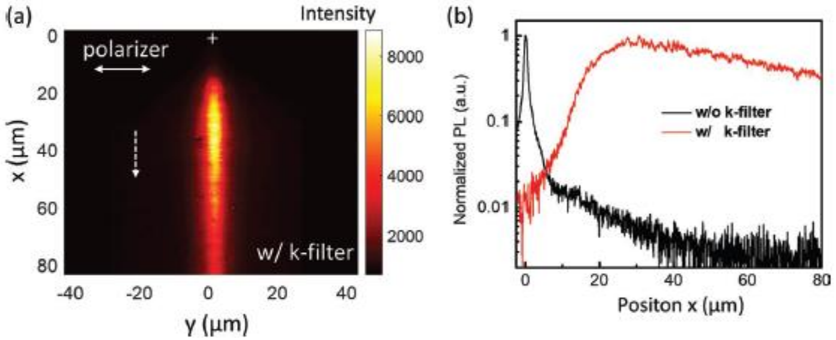
David M. Coles[1†], Niccolo Somaschi[2,3], Paolo Michetti[4], Caspar Clark[5], Pavlos G. Lagoudakis[2], Pavlos G. Savvidis[6,7] and David G. Lidzey[1*]

Polaritons *Angew. Chem. Int. Ed.* **2021**, *60*, 16661 – 16667

Ultralong-Range Polariton-Assisted Energy Transfer in Organic Microcavities

Kyriacos Georgiou, Rahul Jayaprakash, Andreas Othonos, and David G. Lidzey**



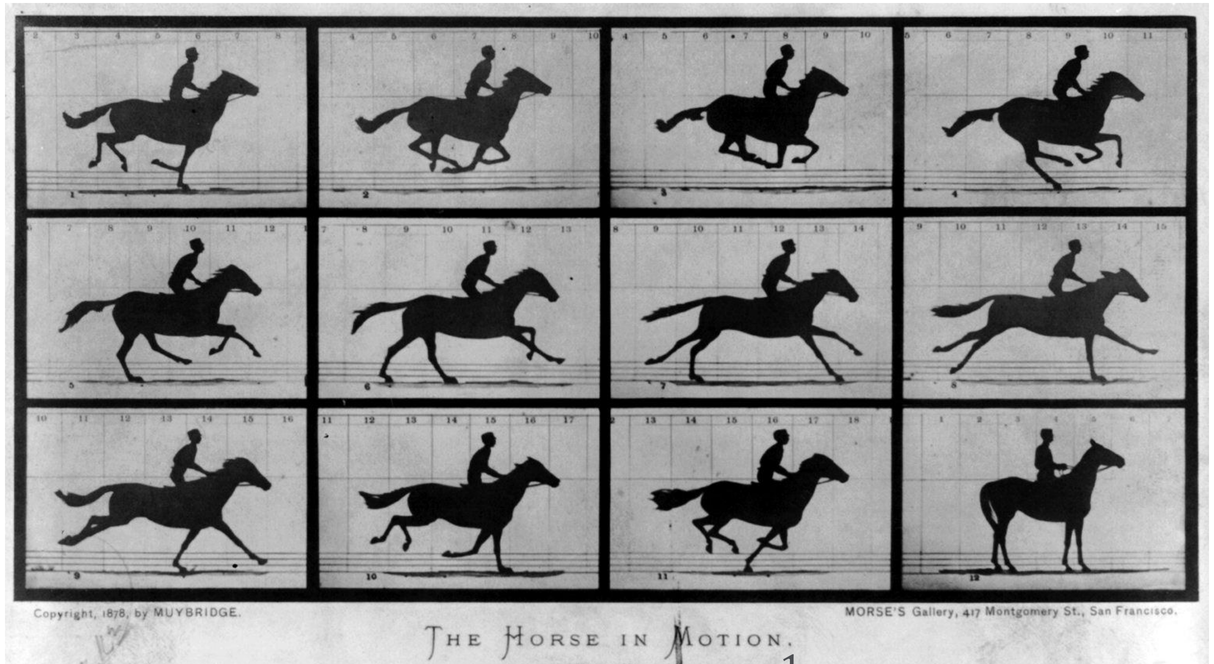


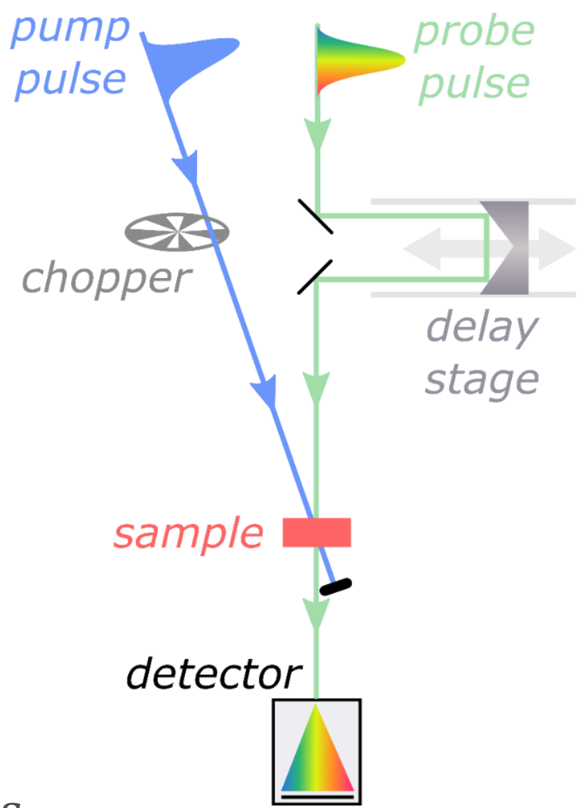
Forrest & Menon, *Adv Mater* 2020

First, some homework

What does an excited exciton-polariton look like?

- Transient absorption/reflectivity yields numerous cavity exciton-polariton fingerprints and surprisingly long lifetimes

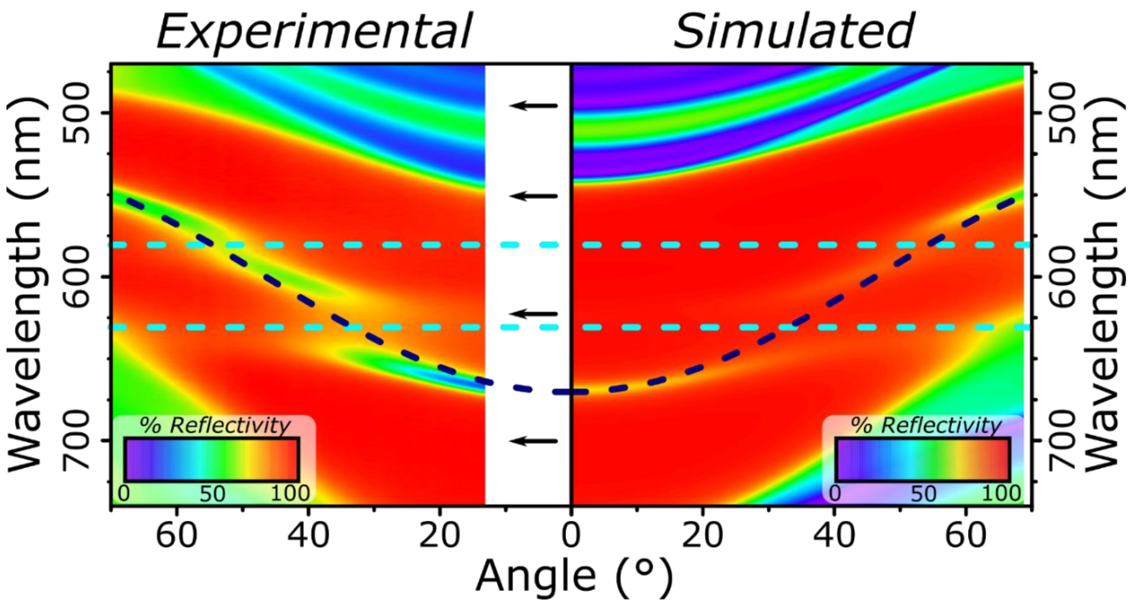


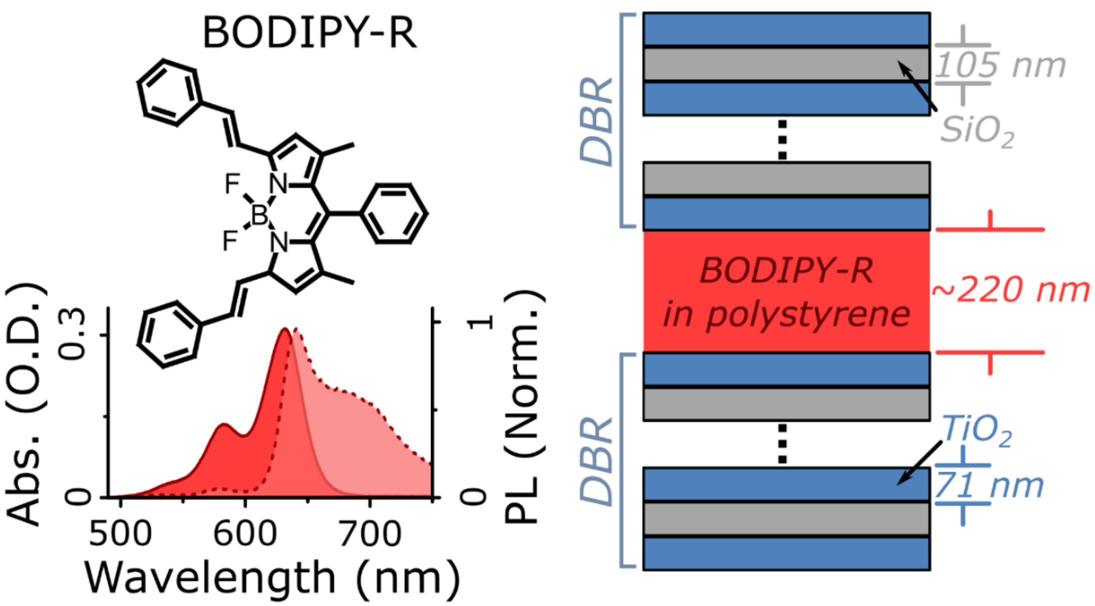


- But $\tau_{polariton} \sim \left(1/\tau_{photon} + 1/\tau_{exciton}\right)^{-1} \sim \left(1/_{10\,fs} + 1/_{10\,ps}\right)^{-1} \sim 10\,fs\ldots$

A model system for polariton dynamics

- Microcavities containing a dispersed, ‘simple’, photostable dye
- Dielectric mirrors for enhanced lifetime and spectral handles



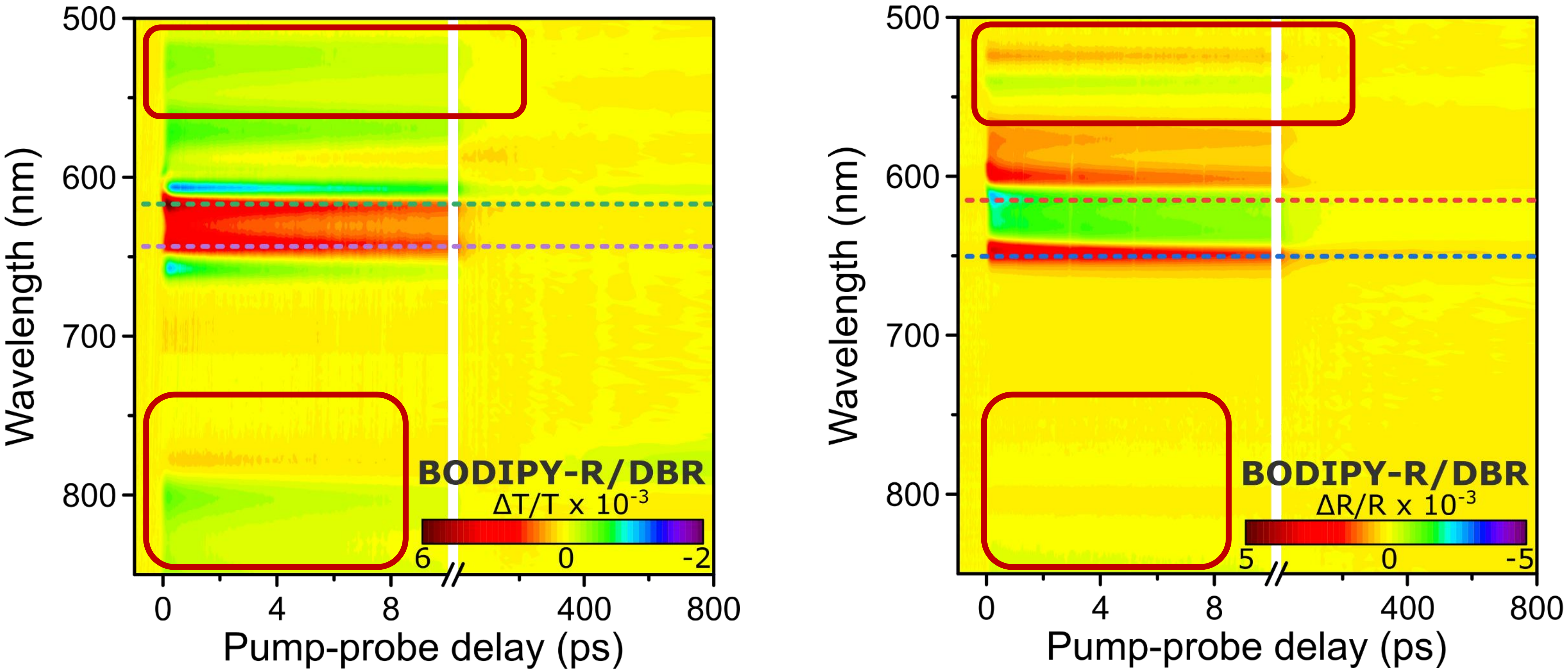


- Single anti-crossing 0-0 exciton absorption
- Energetic structure fully described with transfer-matrix model

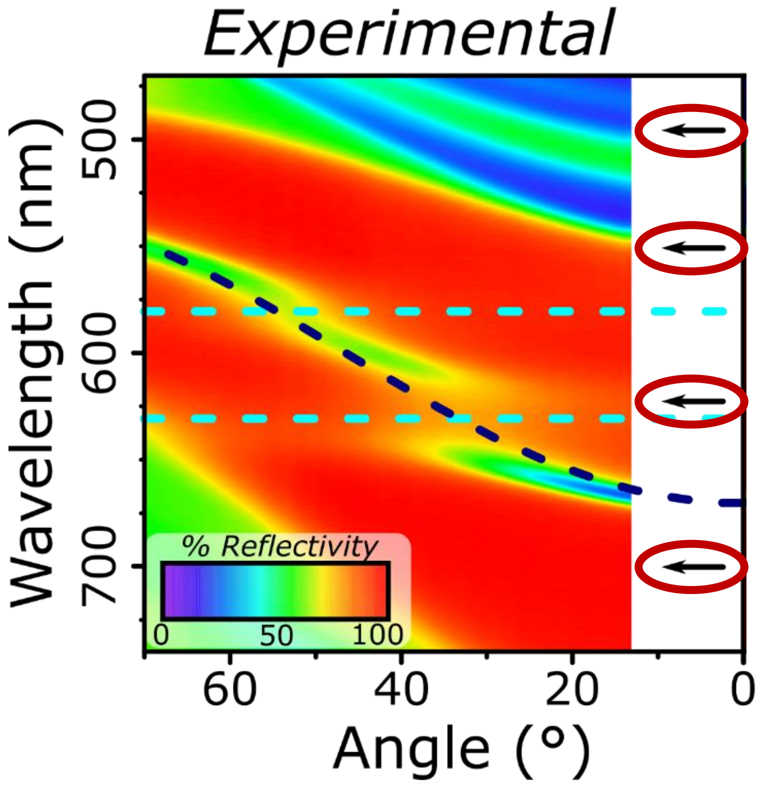
Renken, Pandya… Musser, J Chem Phys 2021

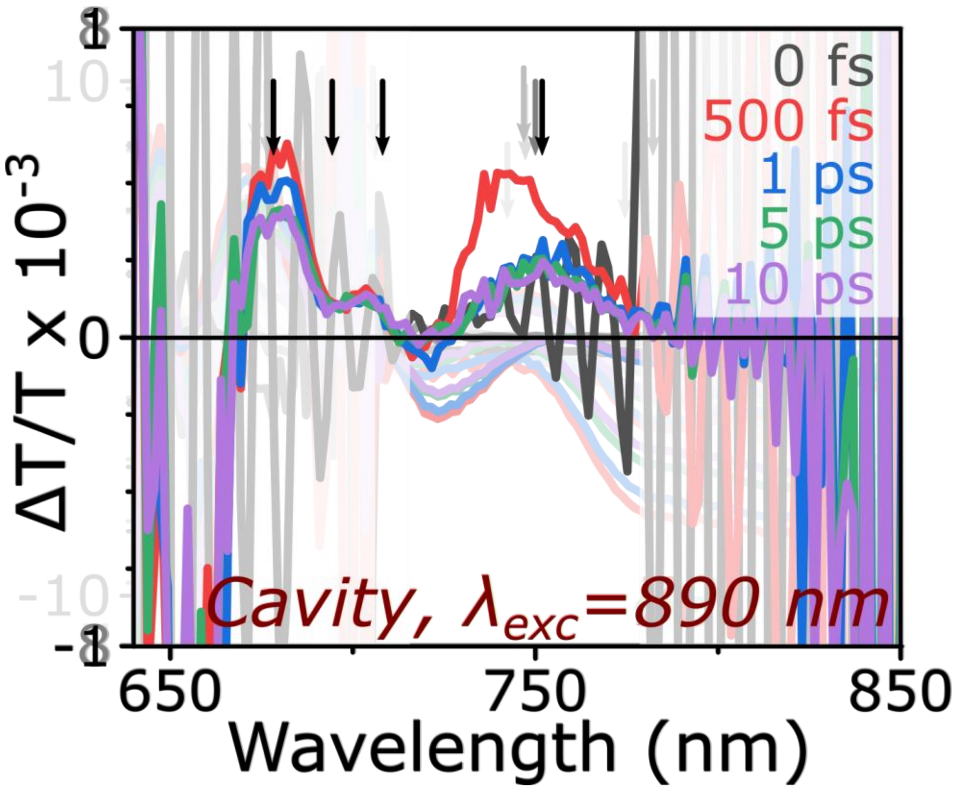
Familiar transient features

- Long-lived derivative response at polariton resonances
- Same behavior captured in absorption and reflectivity



A closer look



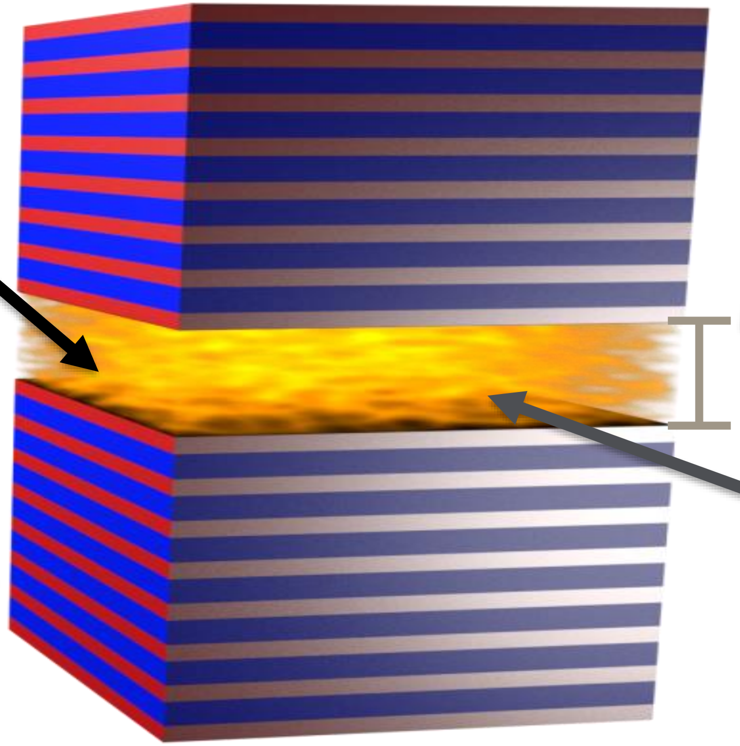


!!!!

Renken, Pandya… Musser, J Chem Phys 2021

Simulating cavity excitation effects 1

- Photoexcitation produces more than just excited electronic states



$\Delta n_{organic}$: *change in background refractive index of organic matrix*

Δn_{DBR}: *change in refractive index of dielectric mirror materials*

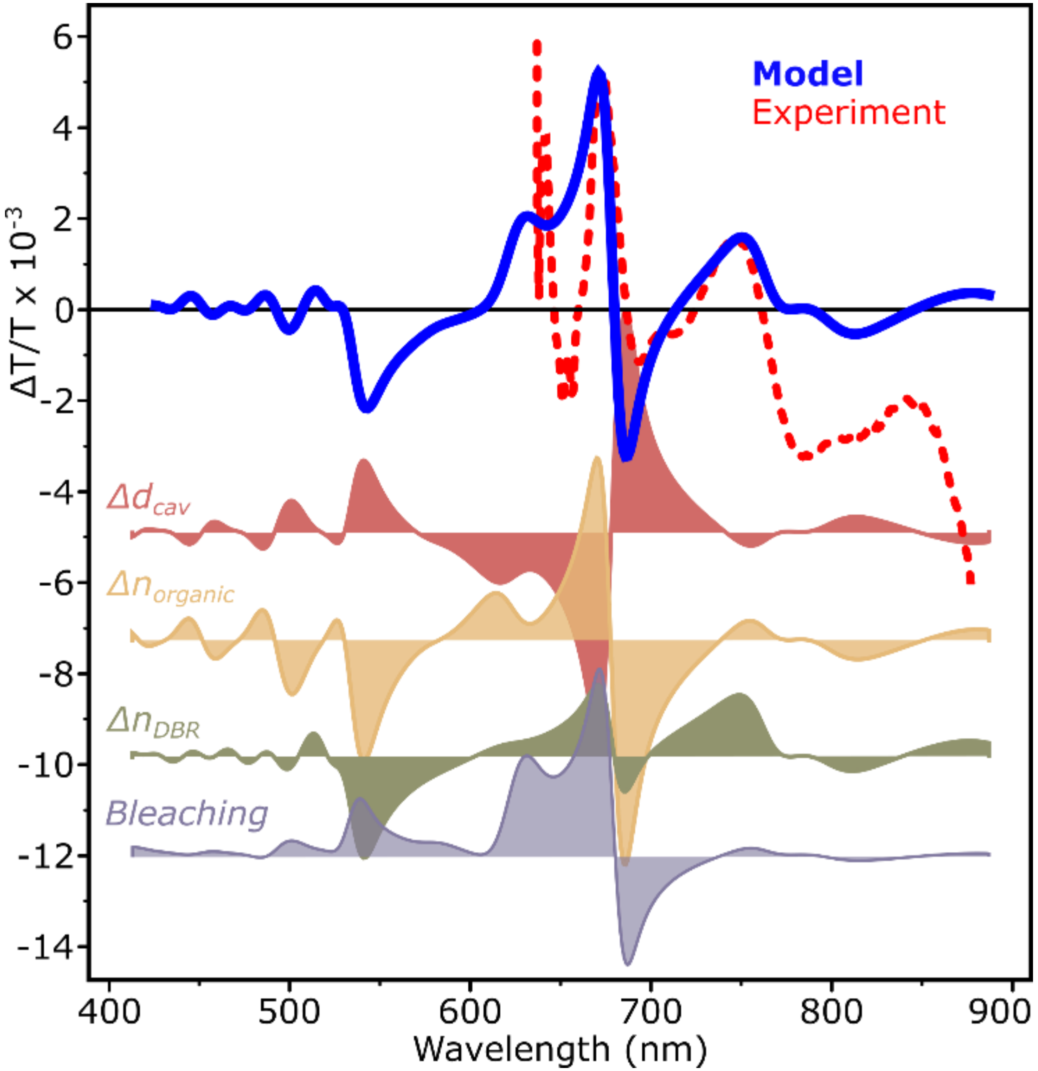
Δd_{cavity}: *thermal expansion following laser pulse absorption*

Bleaching: *removal of ground-state population → reduction of ground-state absorption*

- Incorporate these as static structural changes within optical model

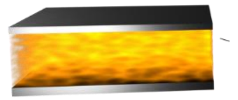
Renken, Pandya… Musser, J Chem Phys 2021

TA simulation from basis states

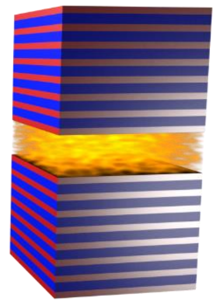


Renken, Pandya… Musser, J Chem Phys 2021

- Crude model captures positions & magnitudes of all spectral features reproduced with λ_{exc}'s
- Have to work harder, and proceed with caution…



Popular
Trivial design
Easy to make + measure
Quick turnaround
τ_{photon} *~ 10 fs*



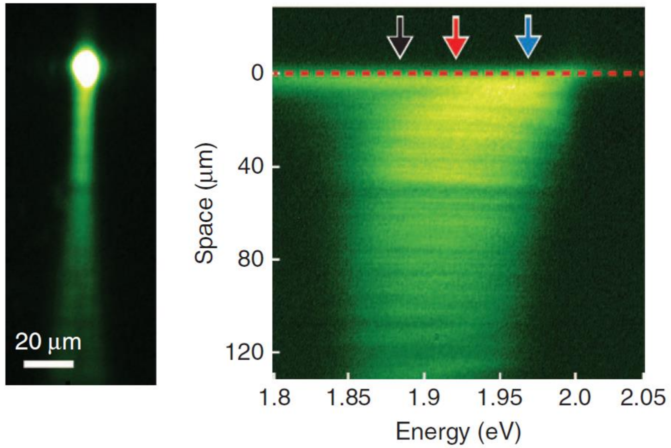
'Rare'
Complex, slow fabrication
Stingy spectral signatures
τ_{photon} ~ 100-300 fs

See further: *Lüttgens et al., ACS Photonics 2022*
& Wu et al., Nature Communications 2022

… and polariton-mediated energy transport?

- Interlayer donor-acceptor transfer well beyond FRET radius

- Intralayer energy transport over 10’s μm



Sanvitto, *Light: Sci & App* 2017

- Rates and states unknown!
- And can we control it?

ARTICLES nature materials
PUBLISHED ONLINE: 4 MAY 2014 | DOI: 10.1038/NMAT3950

Polariton-mediated energy transfer between organic dyes in a strongly coupled optical microcavity

David M. Coles[1†], Niccolo Somaschi[2,3], Paolo Michetti[4], Caspar Clark[5], Pavlos G. Lagoudakis[2], Pavlos G. Savvidis[6,7] and David G. Lidzey[1*]

Polaritons — *Angew. Chem. Int. Ed.* **2021**, *60*, 16661 – 16667

Ultralong-Range Polariton-Assisted Energy Transfer in Organic Microcavities

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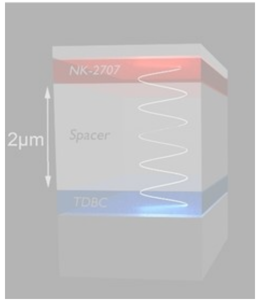
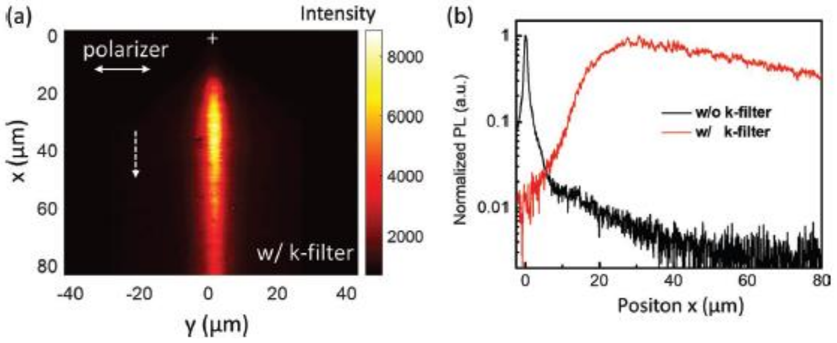
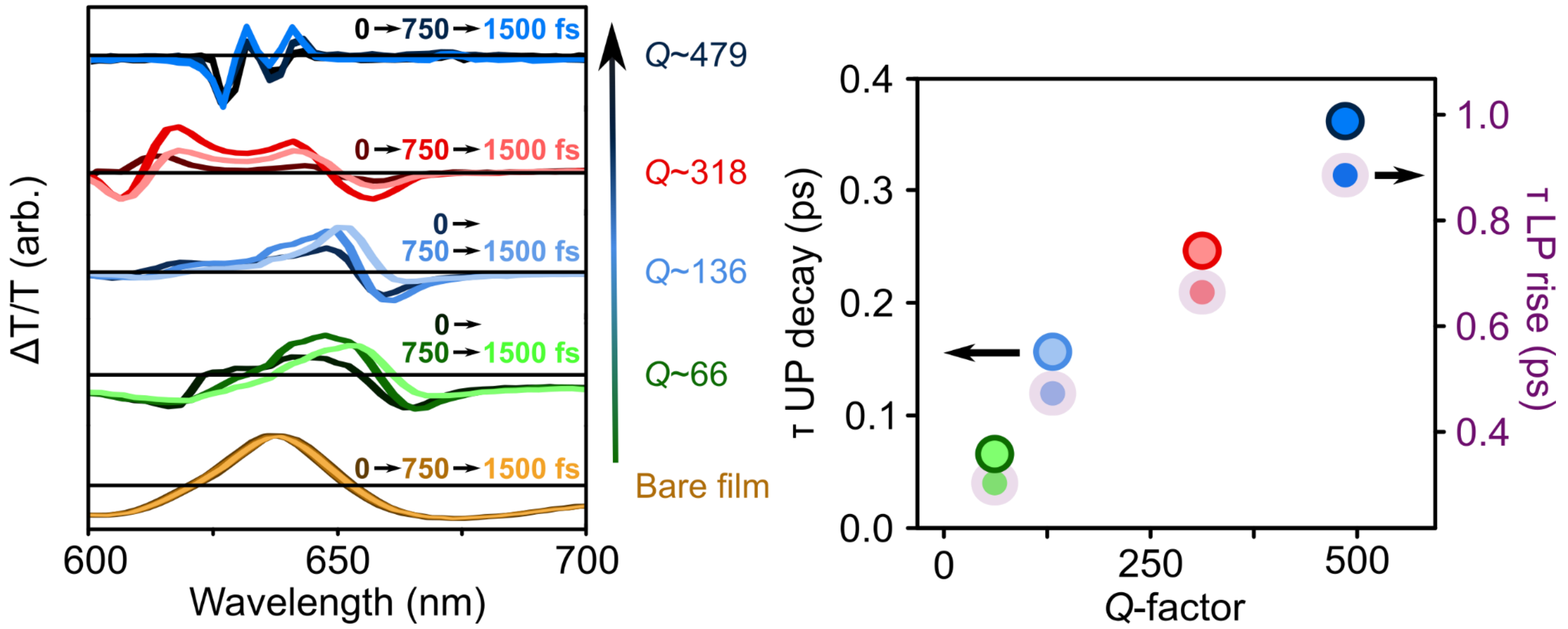




Forrest & Menon, *Adv Mater* 2020

Quick and dirty workaround

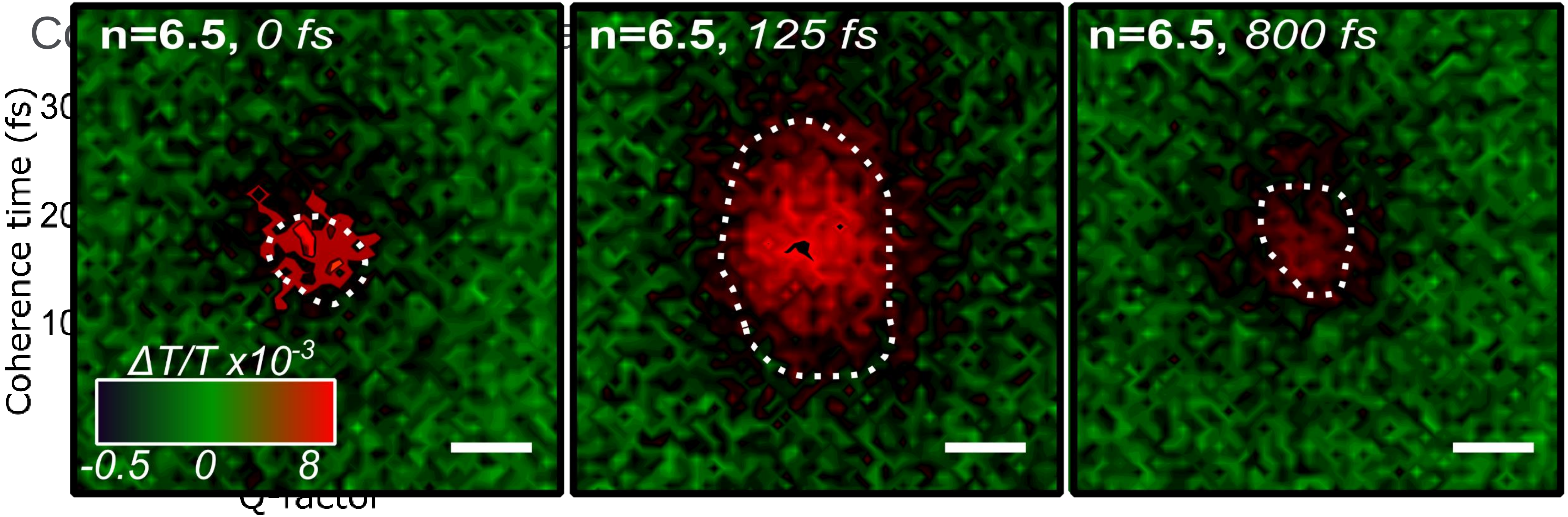
- Related family of BODIPY-R dielectric cavities
- Selectively alter the photonic/polaritonic states by tuning the cavity structure
- Similar long-lived signatures... but part of the features at UP/LP peaks tracks with Q-factor



Pandya… Musser, Advanced Science 2022

Expansion and collapse

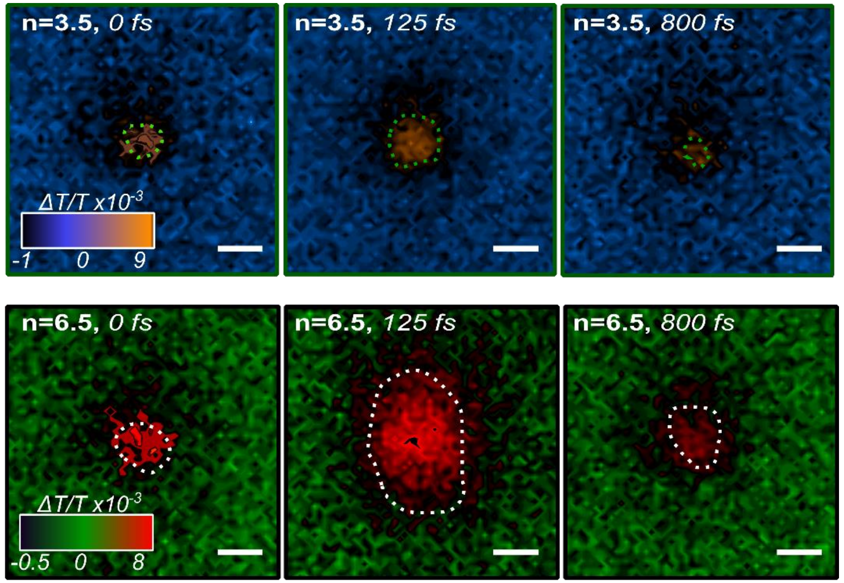
- Track the positive band ~640 nm associated with lower polariton
- Ultrafast expansion followed by return to original size with no further movement → coherent polariton vs reservoir dynamics (*scale bar: 500 nm*)
- C

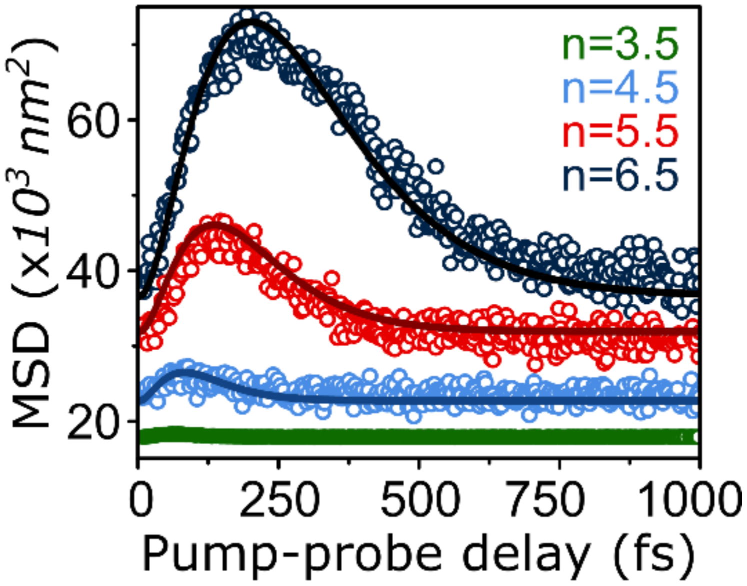


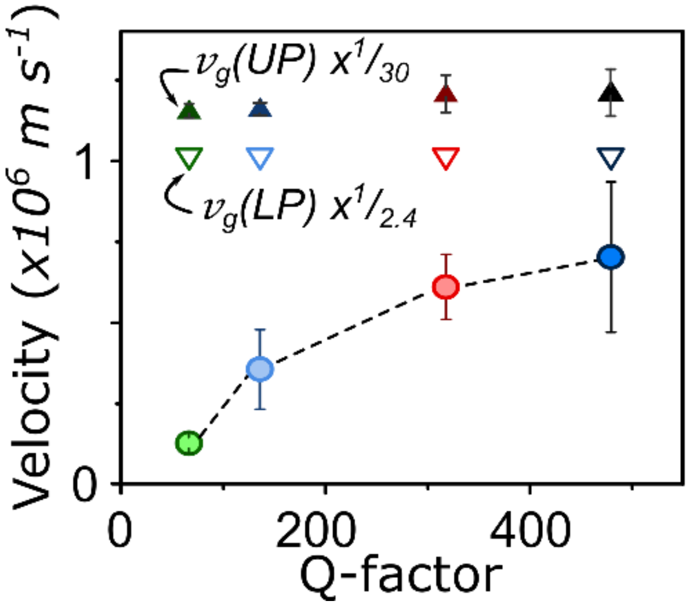
Pandya… Musser, Advanced Science 2022

Ultrafast transport: Q-factor control

- Two population model: coherent polaritons & near-static dark states
- Exceptionally fast transport for organic excitons but slow for polaritons
- Lifetime and range of transport increase with Q-factor… and so does velocity!



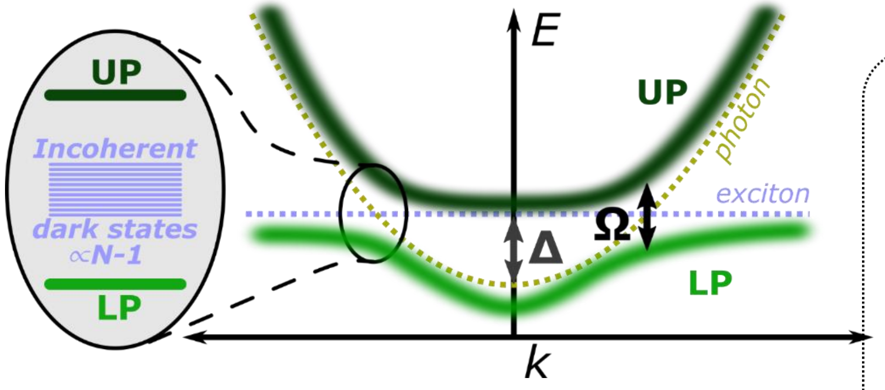


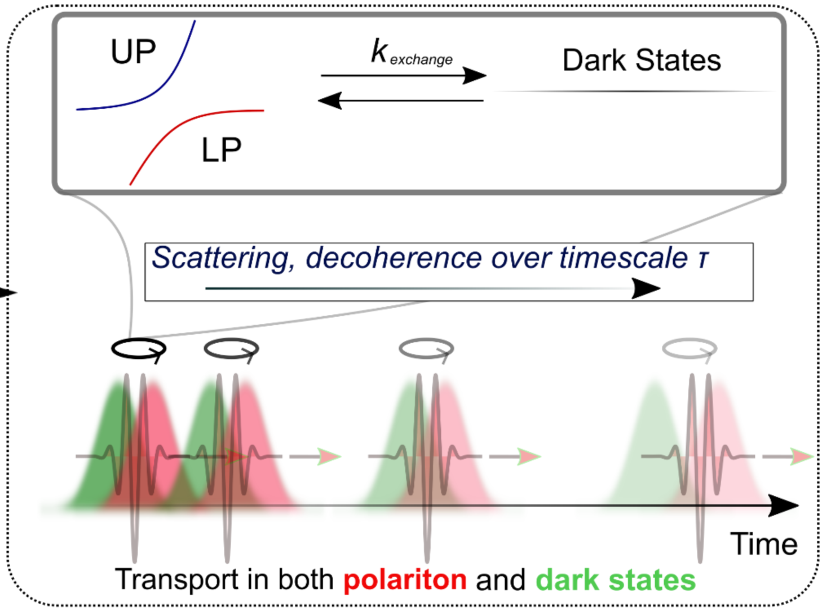


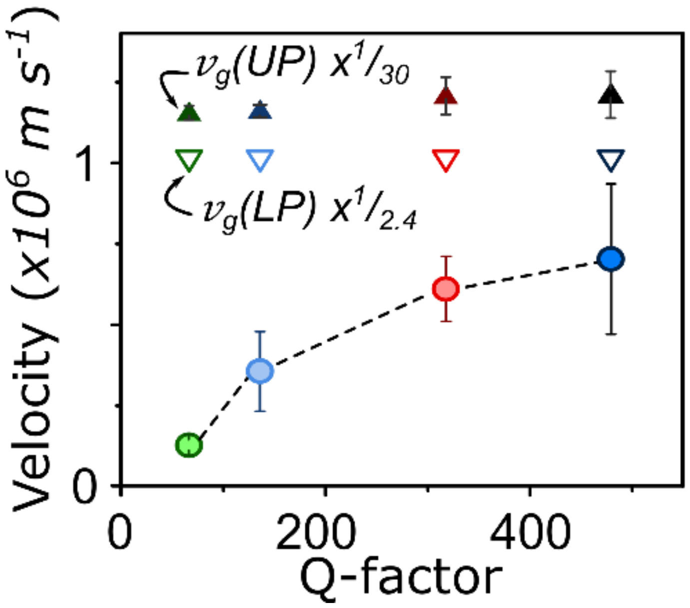
Pandya… Musser, Advanced Science 2022

The EPs are not alone

- Ballistic transport from EPs, and Q-factor sensitivity from dark states
- Demands exceptionally rapid interplay between the bright and dark states
  - Molecular states serve as a brake & reservoir for longer-lived transport
  - *Do they provide a new avenue for control?*

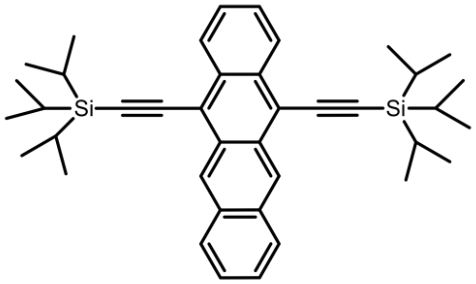




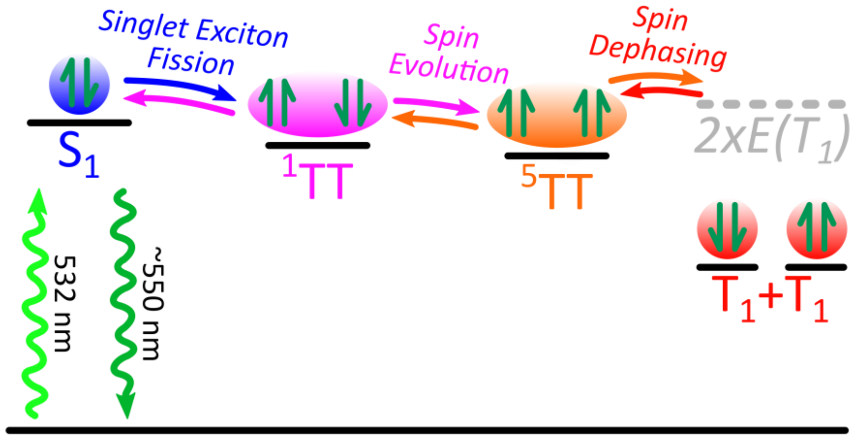


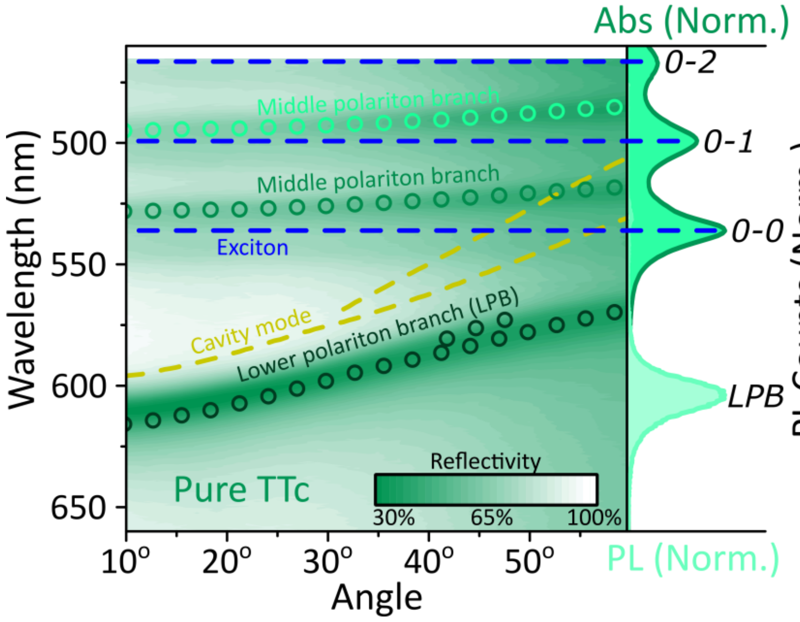
Pandya… Musser, Advanced Science 2022

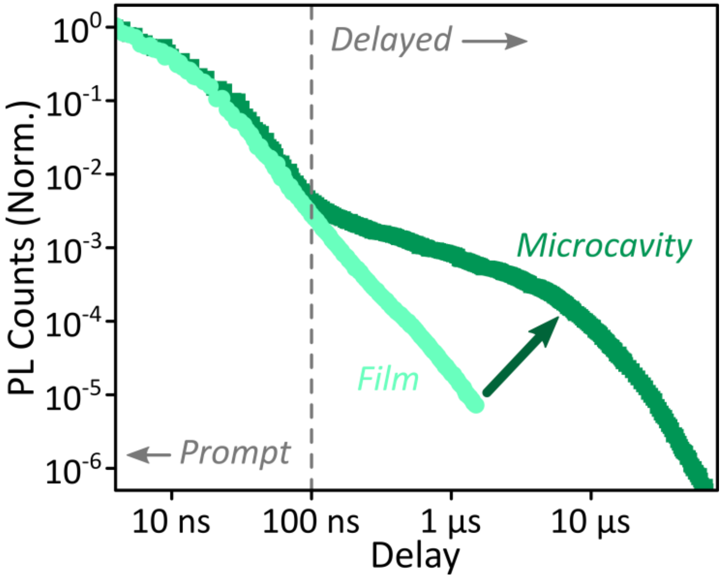
Another kind of ‘dark’: Triplet-pair states



5,12-bis(triisopropylsilylethynyl) tetracene: **TTc**







Polak… Musser, Chem Sci 2020

- Polariton formation vastly increases delayed emission in TIPS-tetracene
- Timescales correspond with ^5TT state… dark state turned bright!
- *Mediated by vibronic state mixing*

See also

Polariton-modified RISC:

Stranius *et al.*, *Nat Commun* 2019

Yu *et al.*, *Nat Commun* 2021

Polariton-modified TTA:

Berghuis *et al.*, *Adv Func Mater* 2019

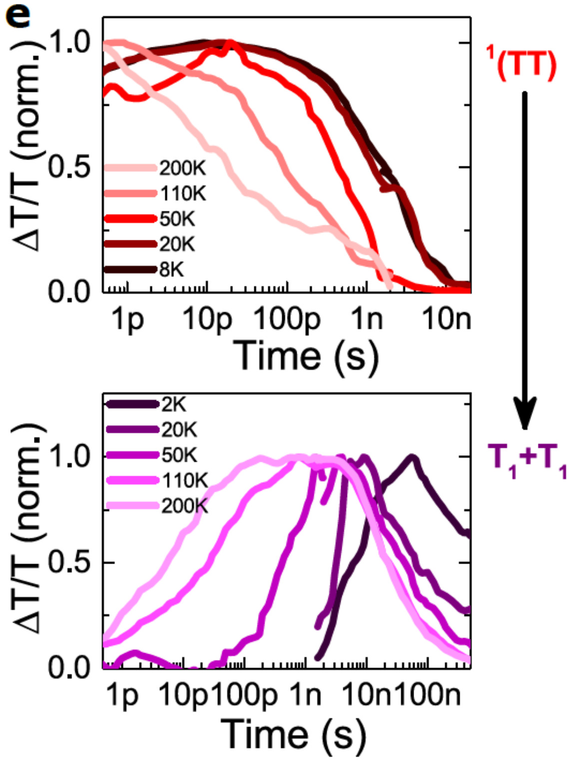
Ye *et al.*, *JACS* 2021

Hard to pick apart

Received 21 Mar 2017 | Accepted 17 May 2017 | Published 12 Jul 2017 DOI: 10.1038/ncomms15953 OPEN

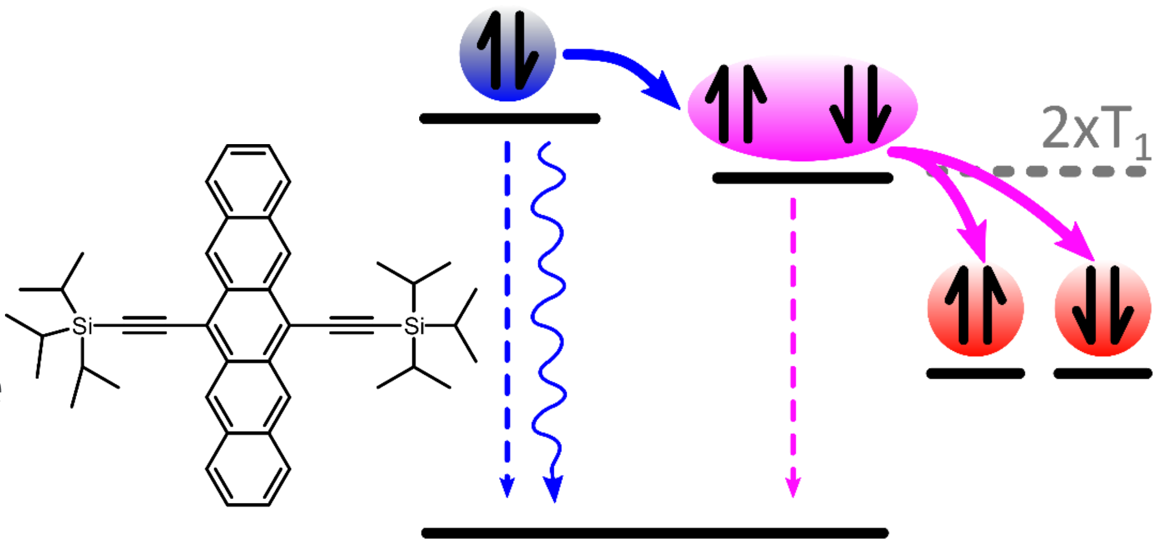
The entangled triplet pair state in acene and heteroacene materials

Chaw Keong Yong[1,2], Andrew J. Musser[1,3], Sam L. Bayliss[1], Steven Lukman[1], Hiroyuki Tamura[4], Olga



- **Exothermic TPc:** SF is unidirectional into a dark ^{1}TT state

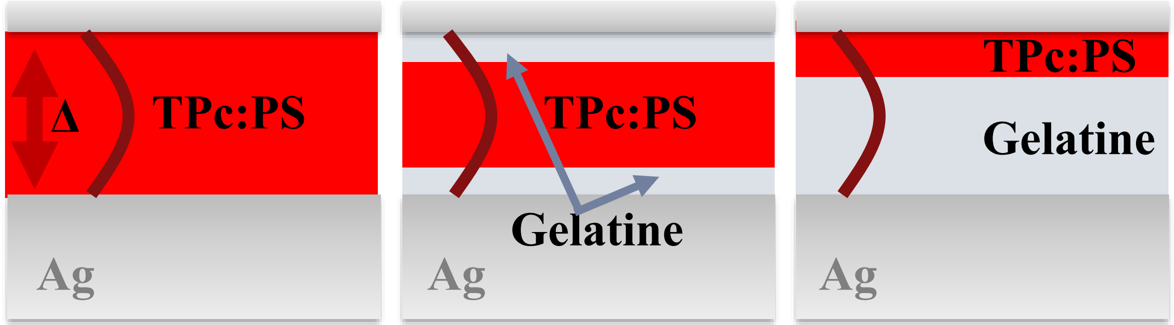
- ^{1}TT is very weakly bound
- Can be stabilised at low temperature



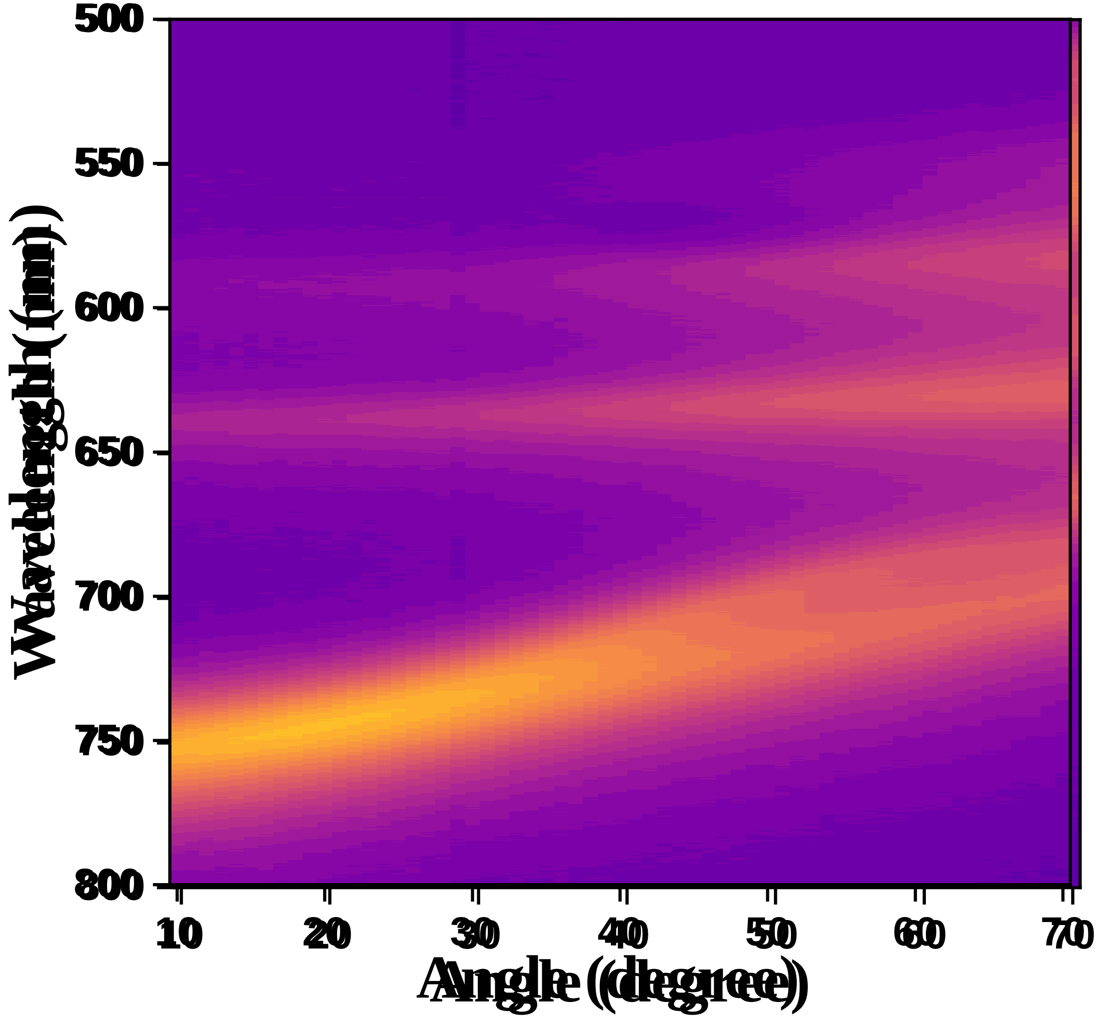
Mukherjee et al., in preparation

Strong coupling to TIPS-Pc

- Smooth, solution-like TPc films with 20% polystyrene
- Widely tuned polariton energies sweep across the molecular energetic structure



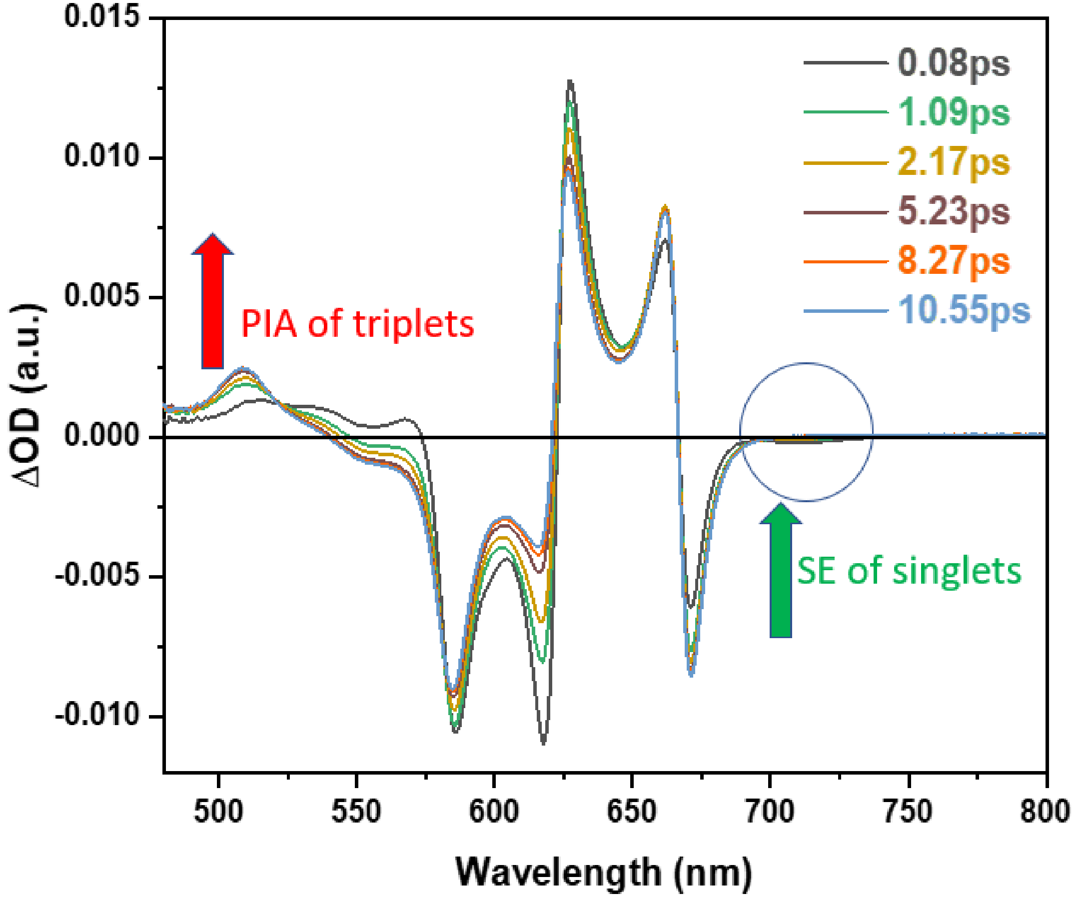
Strong coupled — *'Protected' strong coupled* — *Weakly coupled*

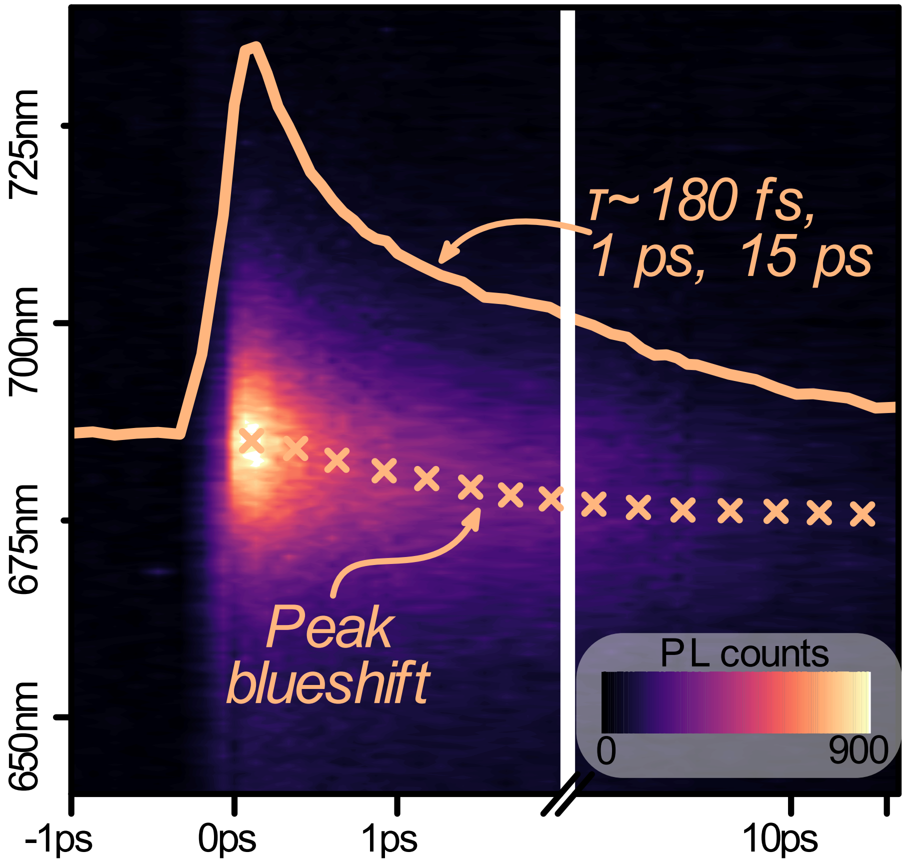


Mukherjee et al., in preparation

SF in TPc cavities

- Quantitative singlet fission <2 ps

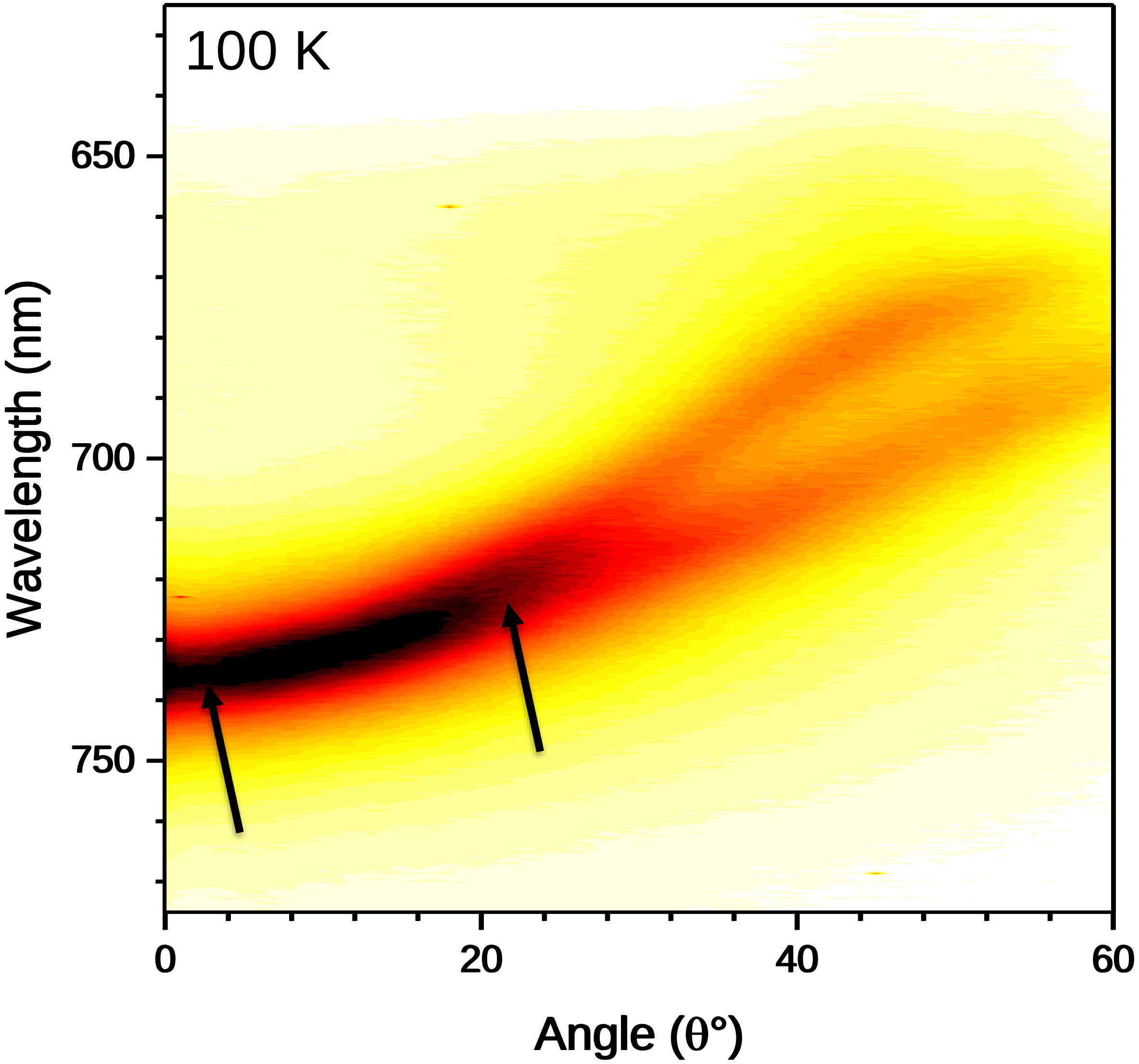




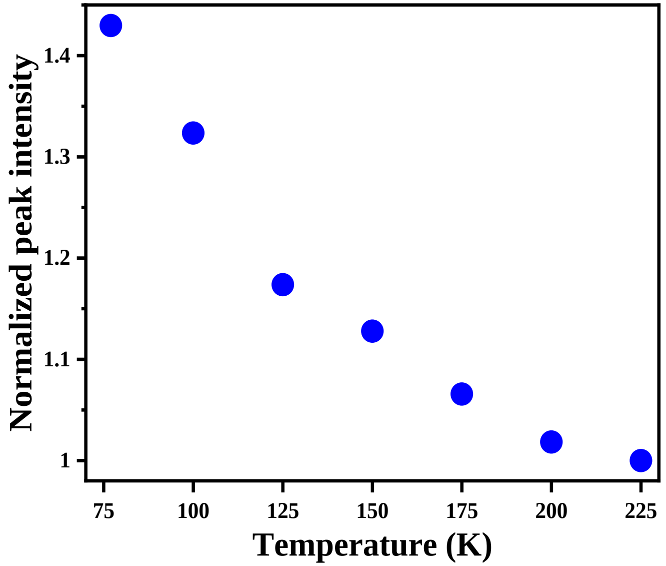
Mukherjee et al., in preparation

Cavity TA: Renken… Musser, J Chem Phys 2021

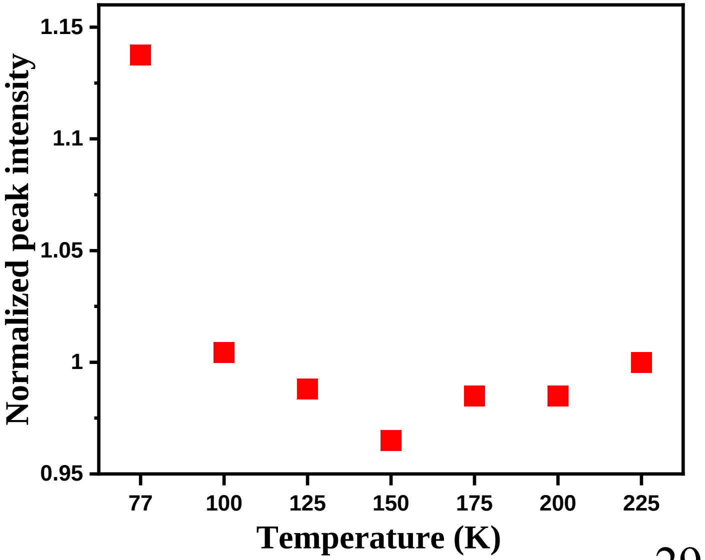
Temp-dependent polariton population



Singlet-tuned cavity



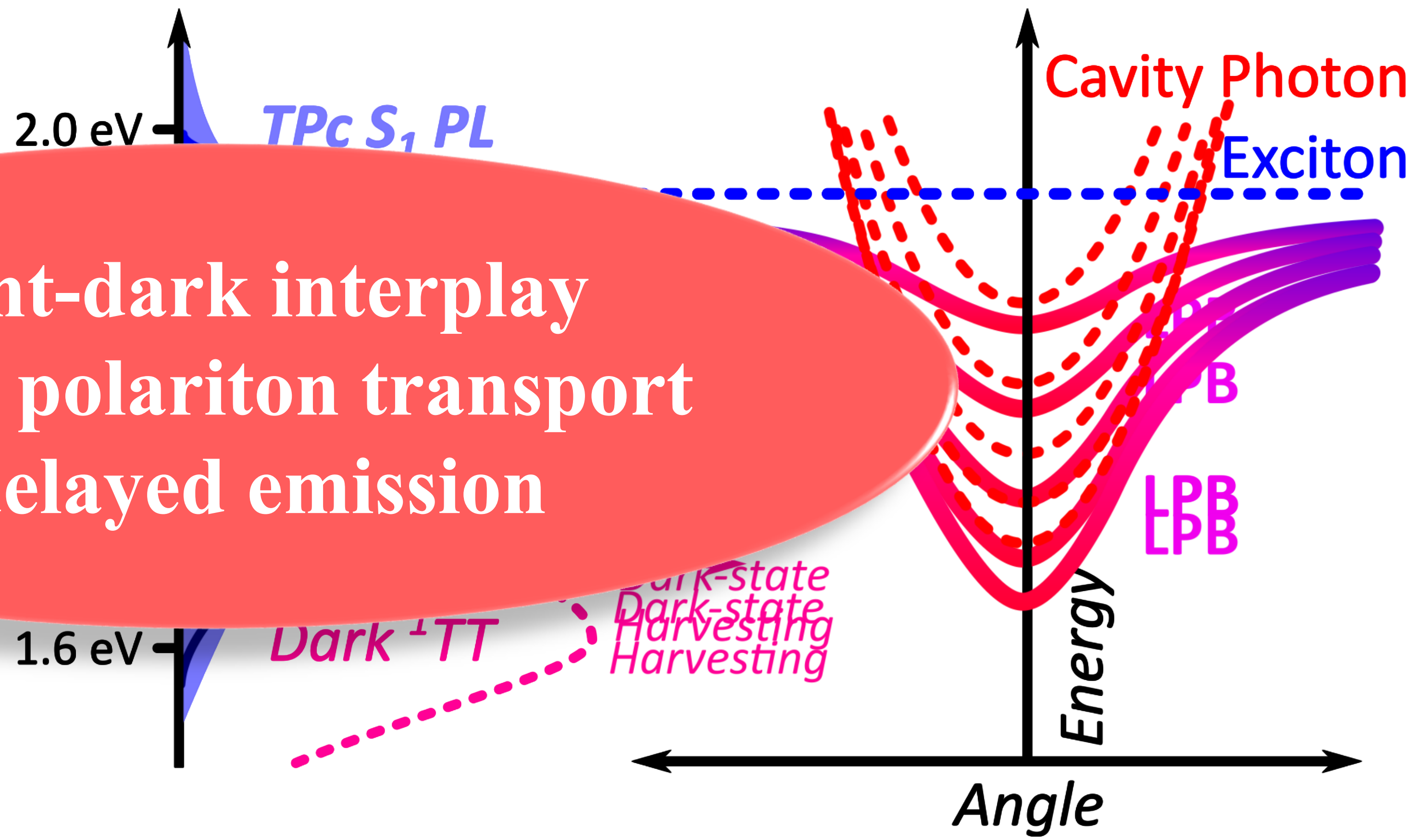
750 nm cavity



Mukherjee et al., in preparation

Resonance with fully 'dark' ^{1}TT

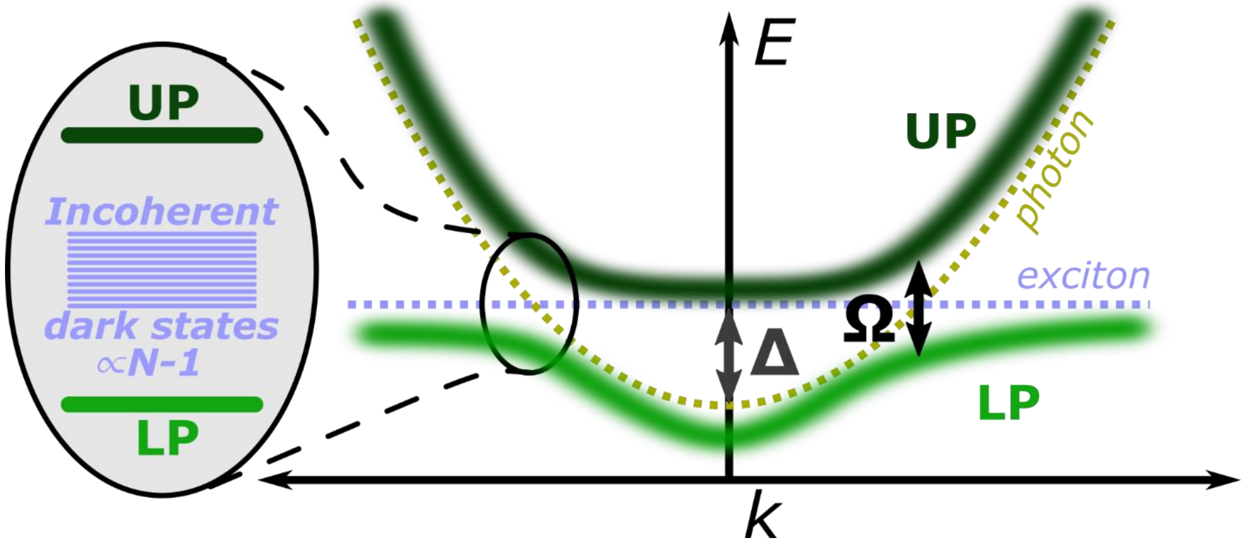
- T-dep at higher energies follows fil
- T-dep at detunings reported ^{1}TT be
- Dark state resonance as a tool to map out energetic structure?

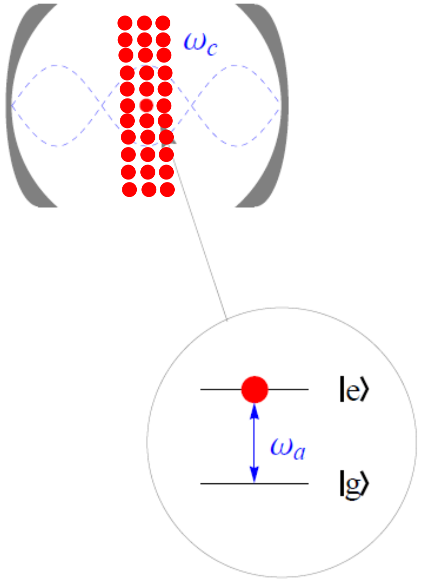


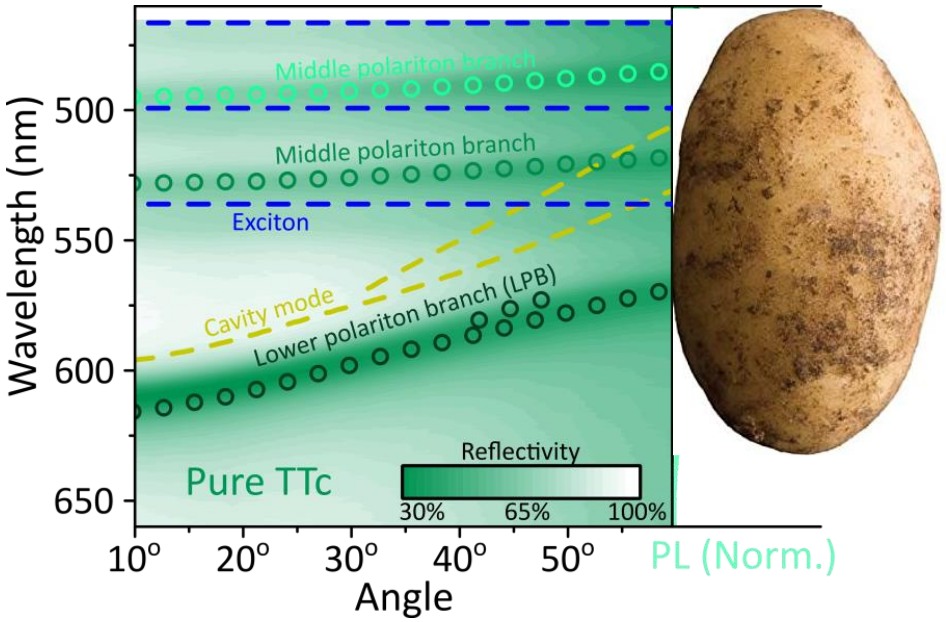
Bright-dark interplay governs polariton transport & delayed emission

Mukherjee et al., in preparation

How dark is dark?

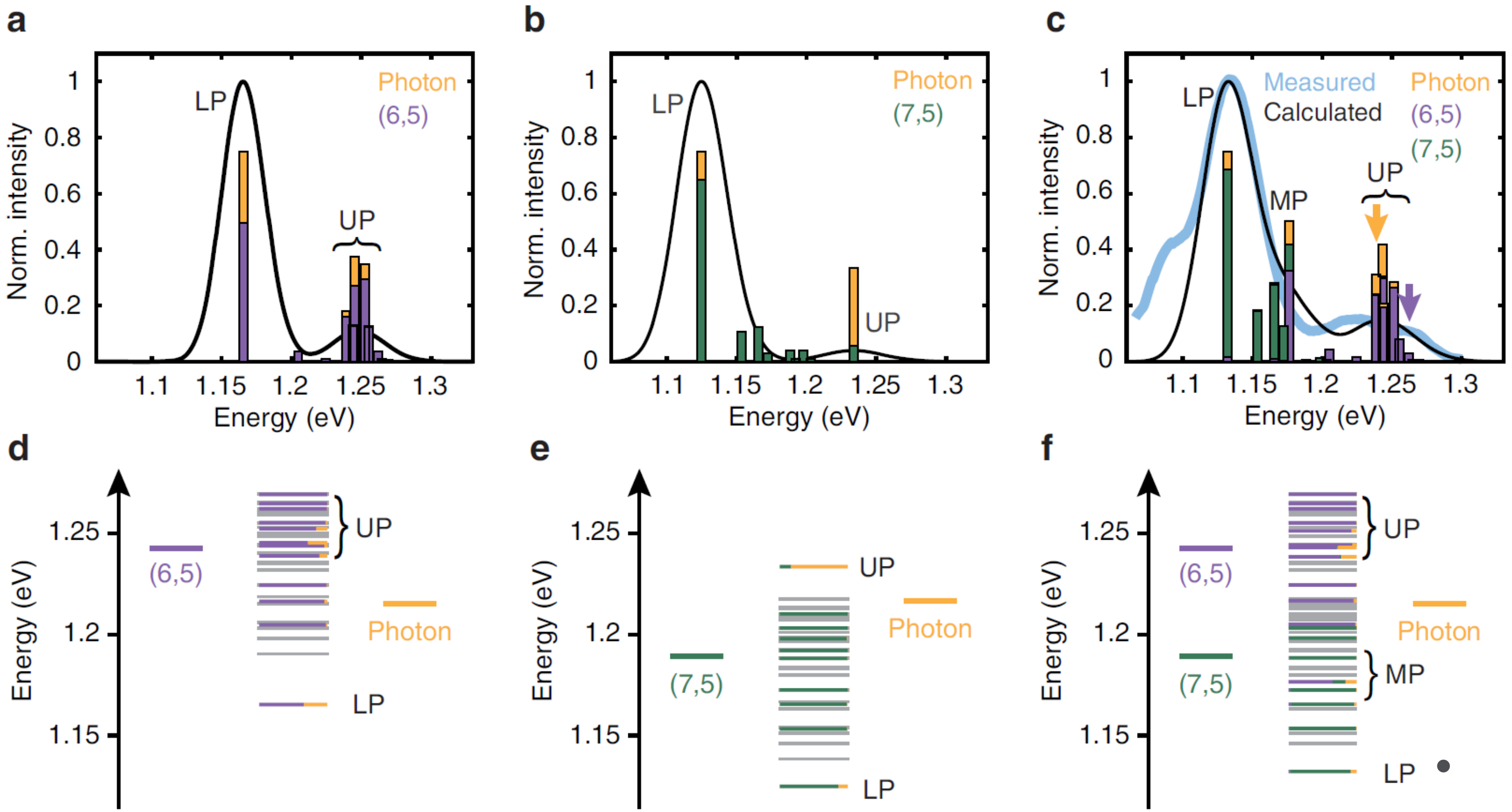




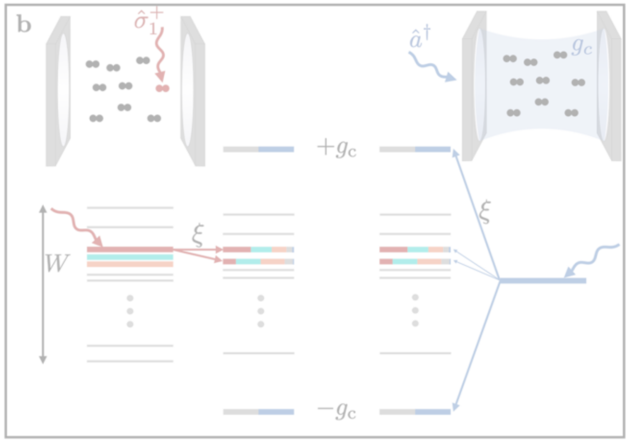


- Intracavity ‘reservoir’ states formally dark in Tavis-Cummings model
- Vibronic peaks give a ladder of polaritons
- … but what if the ‘excitons’ aren’t so tidy?

Disorder effects in model systems

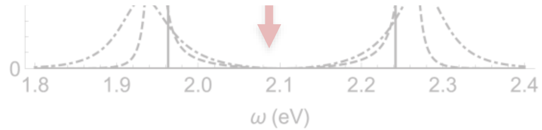


Son *et al.*, Nat Commun 2022



Wellnitz *et al.*, Comm Phys 2022

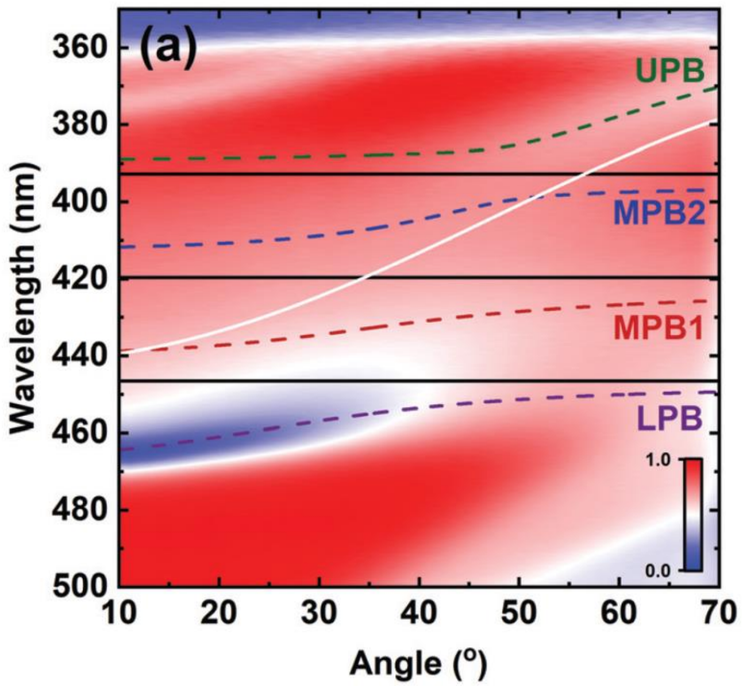
igenstates scrambled → nhanced entanglement!

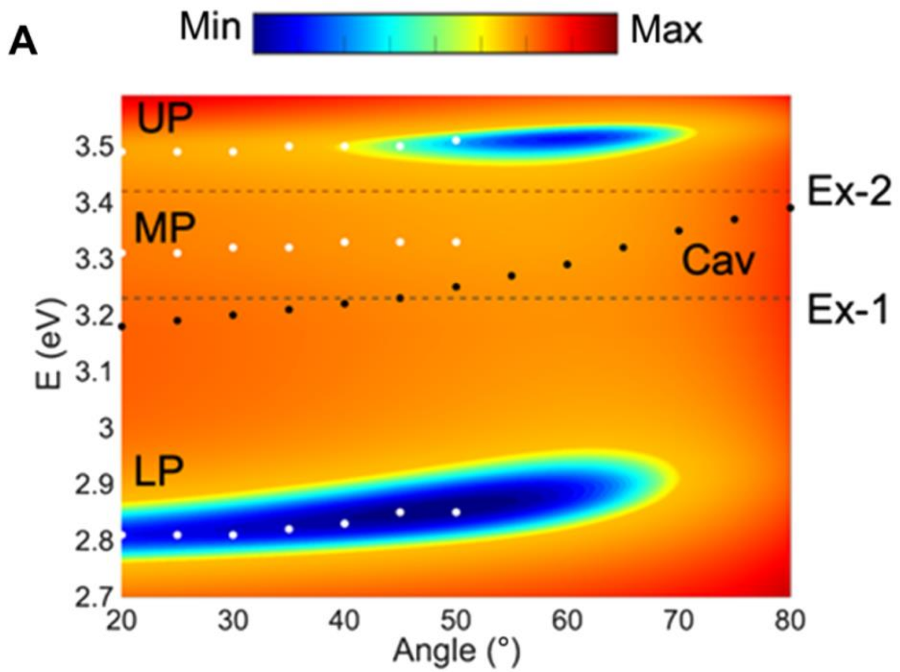


Gera & Sebastian, J Chem Phys 2022

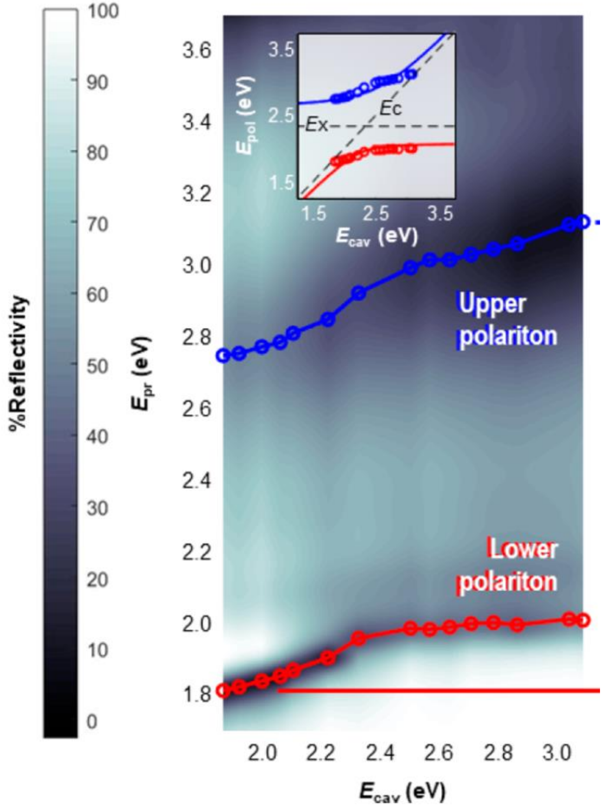
- New relaxation/energy transfer pathways?

Missing middle polaritons?





P3HT: A tunable platform for missing MPs?

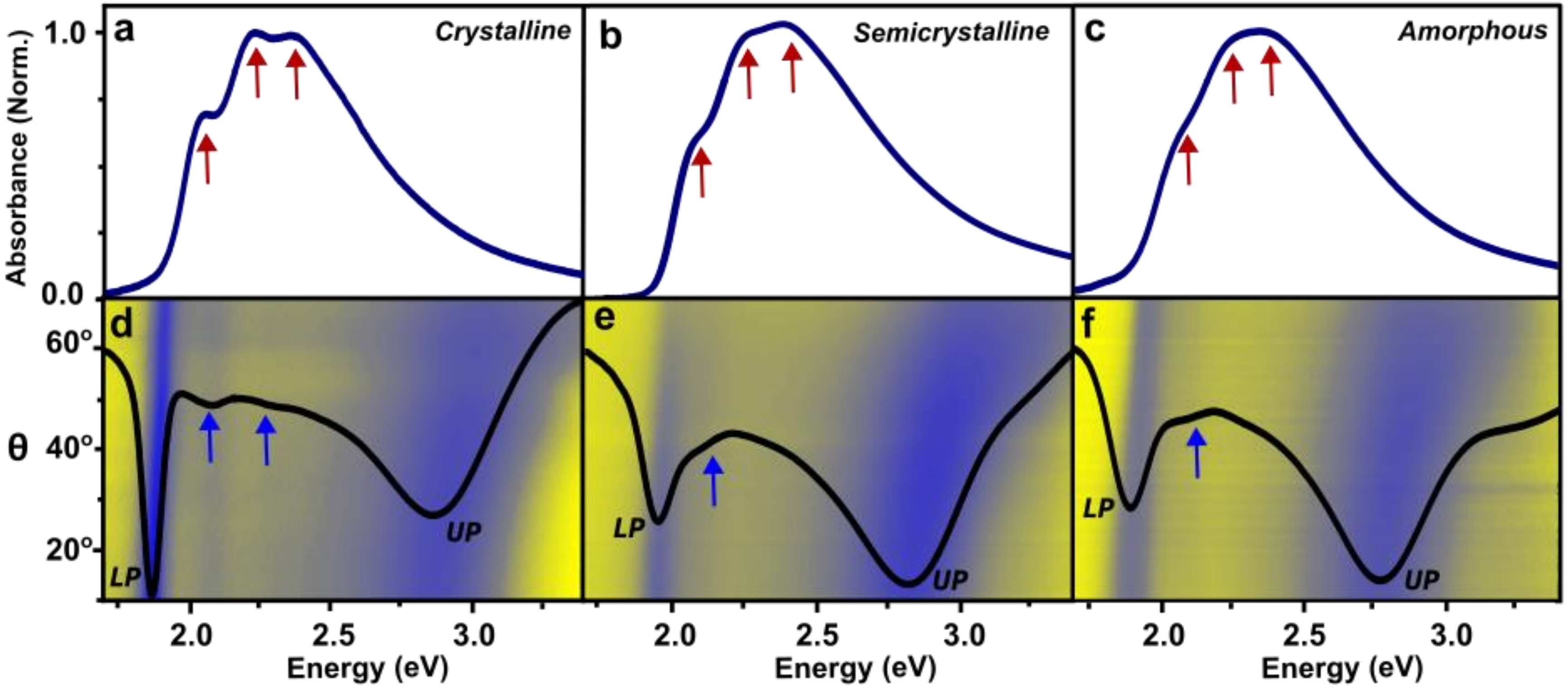


DelPo et al., JPCL 2021

- Broad absorbers show fewer 'bright' polariton states than the vibronic ladder picture suggests
- … but still analyzed in that framework!
- Is there a better way to describe them?

Tunable excitons & EPs in P3HT

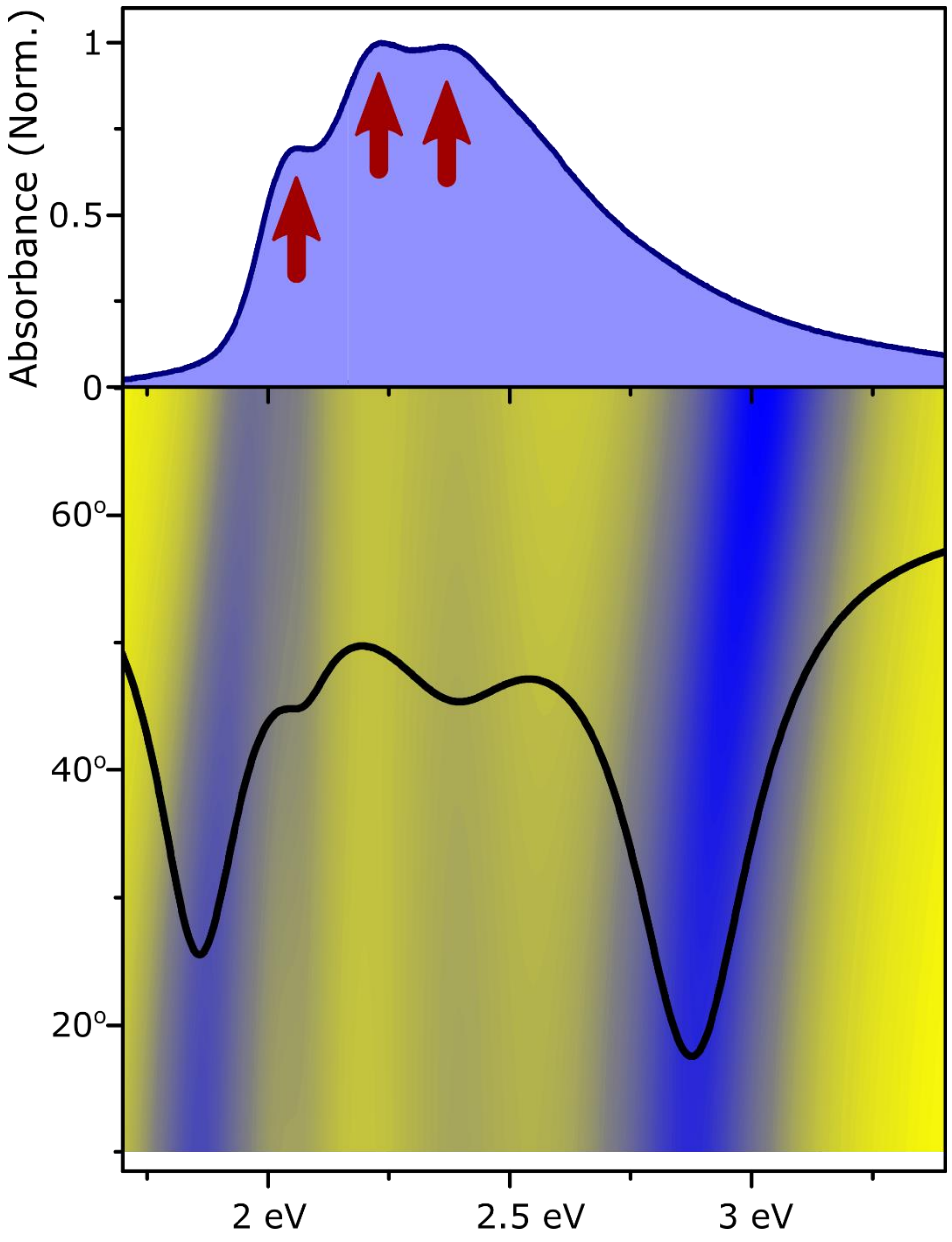
- Control interchain packing with solvent, concentration, spin speed
- Same type & number of chains in all cavities, simply vary linewidth
- Different intermediate modes evident → not captured in standard models



George et al., under review (arXiv: 2309.13178)

Standard model

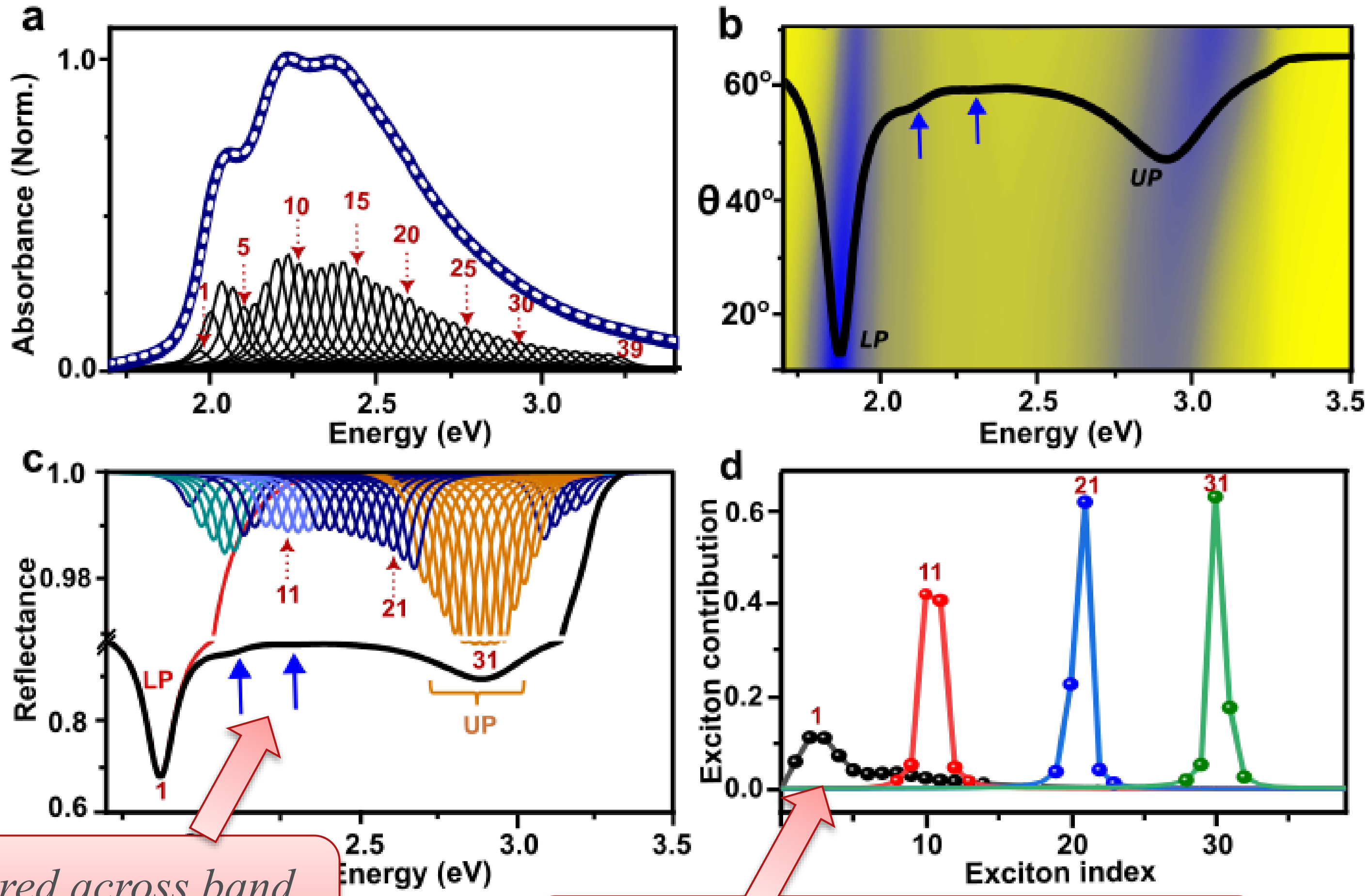
- Incorporate linewidths into coupled-oscillator model to get reflectance
- ‘3-oscillator’ model captures positions of UP, LP & intermediate bands
- Strongly overestimates intensity of middle bands
- Does not distinguish between film types



George et al., under review (arXiv: 2309.13178)

Beyond the standard model

- Simple ‘multi-oscillator’ decomposition to explicitly account for electronic disorder
- Closely captures weak bands & material dependence
- New insight into electronic structure of bright vs. ‘dark’ states under strong coupling
- *What does it mean for EP relaxation & transport?*



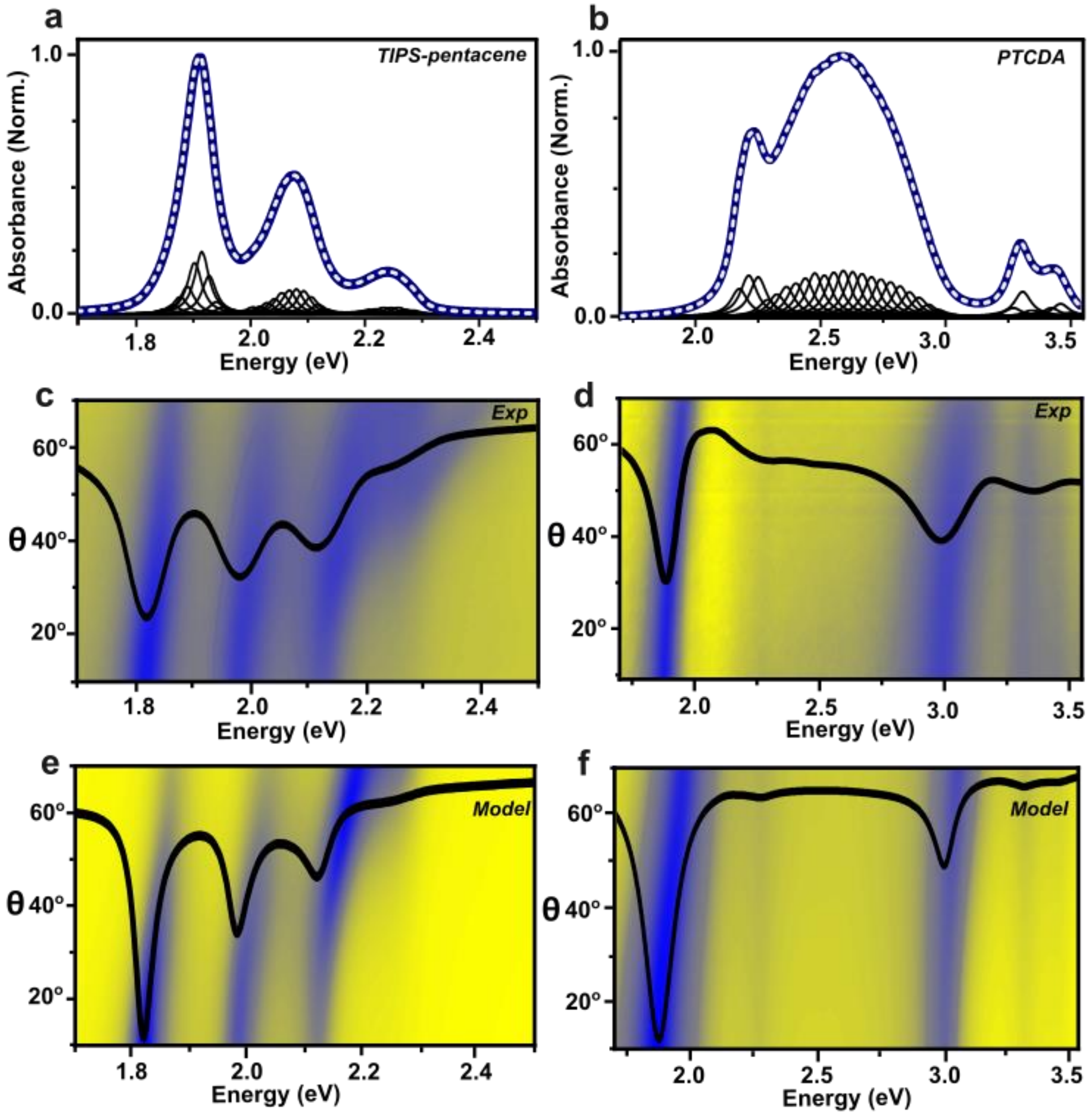
*Photon character widely shared across band between EPs → **dark states become ‘gray’***

EPs & gray states are mixed, but contributions are energetically local

George et al., under review (arXiv: 2309.13178)

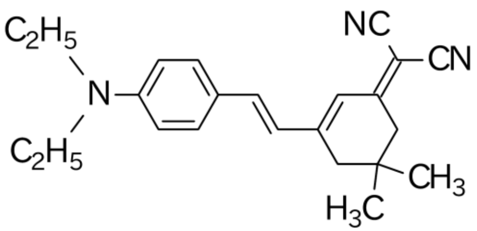
A versatile tool

- Readily captures the coupling behavior of any organic, from ordered to disordered, on the same footing
- Recovers clean Tavis-Cummings-like result with narrow absorbers
- Related continuum strong-couping model: *Gunasekaran et al., arXiv:2308.08744*

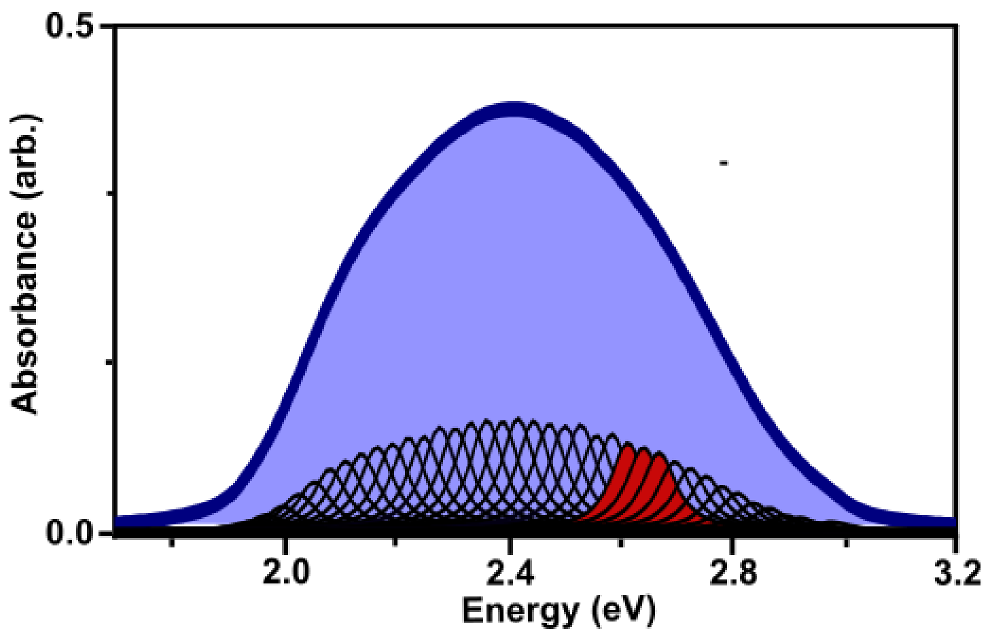


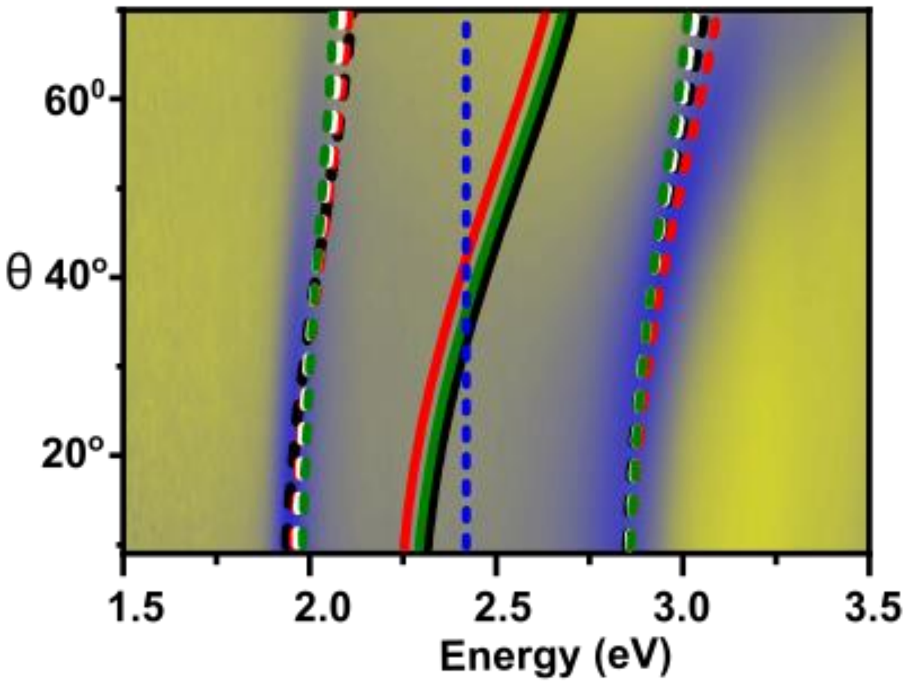
George et al., under review (arXiv: 2309.13178)

Ultrastrong coupling reconsidered



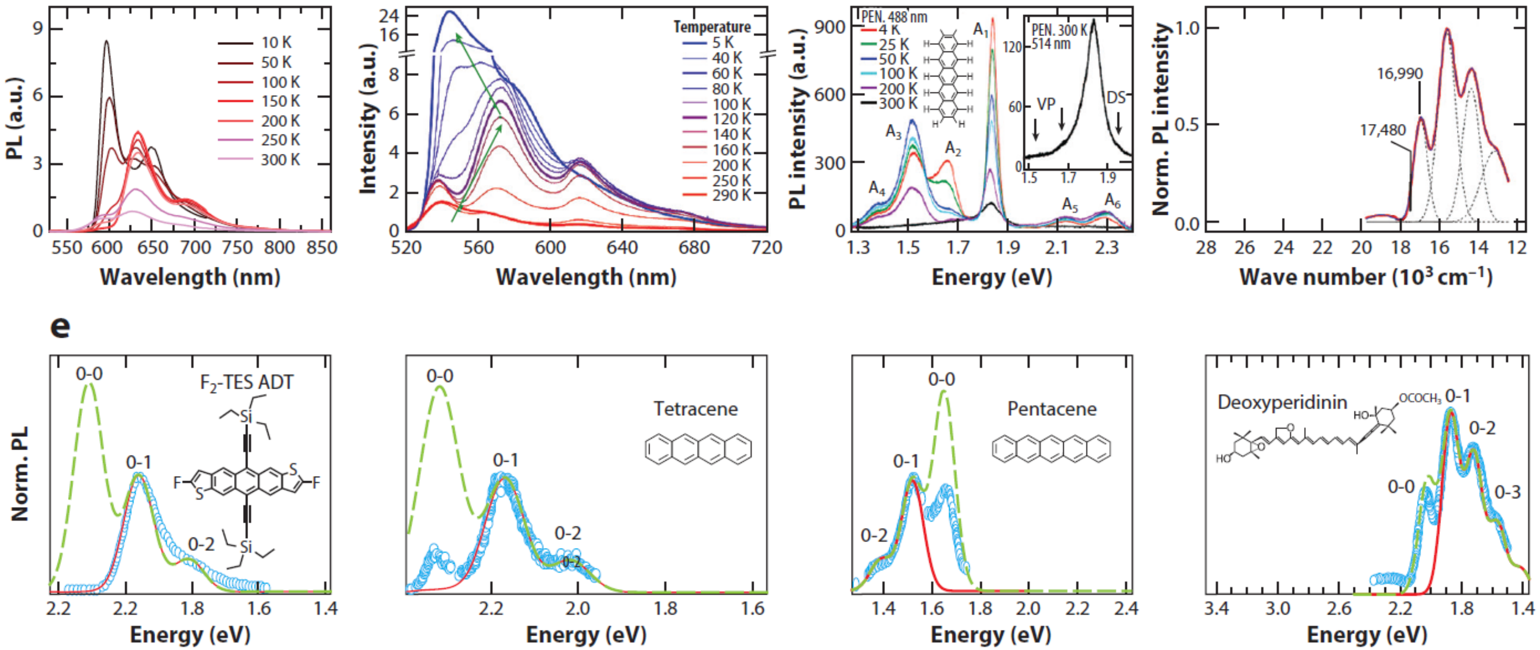
- Model readily captures ultrastrong coupling with enormous splittings ~1.25 eV
- But none of the ‘ultrastrong’ physics are needed to do so
- Large splittings imposed by collective coupling over large linewidth





George et al., under review (arXiv: 2309.13178)

How dark is dark? The sequel…



Musser & Clark, Annu Rev Phys Chem 2019

nature chemistry
ARTICLES
https://doi.org/10.1038/s41557-020-00593-y
Check for updates

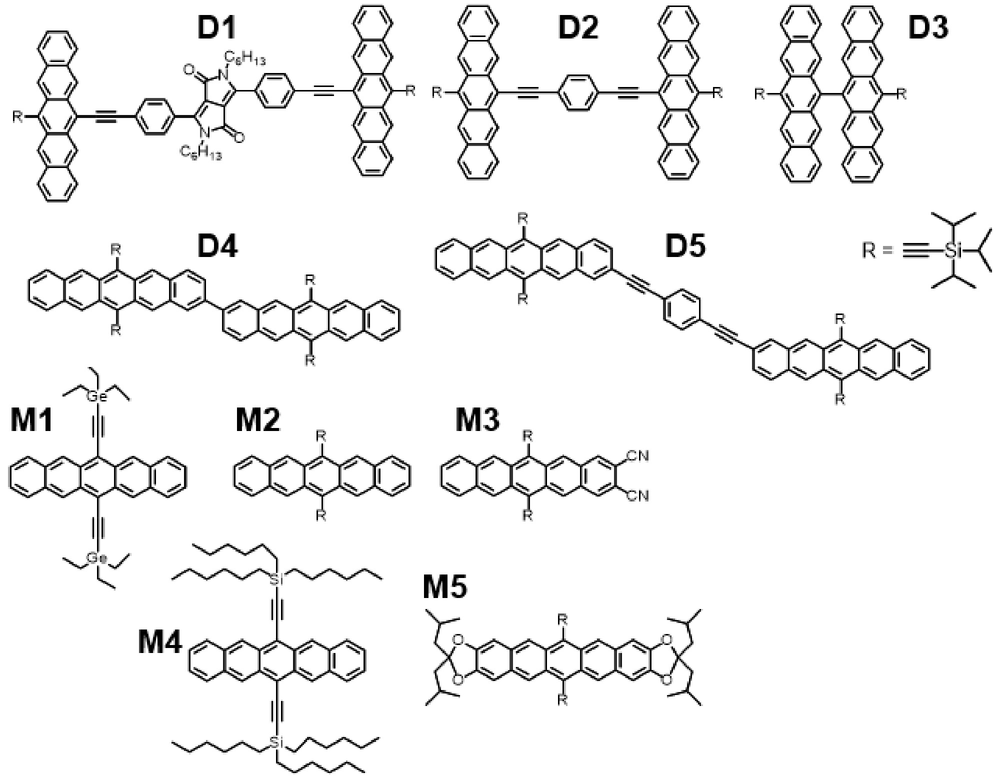
Emissive spin-0 triplet-pairs are a direct product of triplet–triplet annihilation in pentacene single crystals and anthradithiophene films

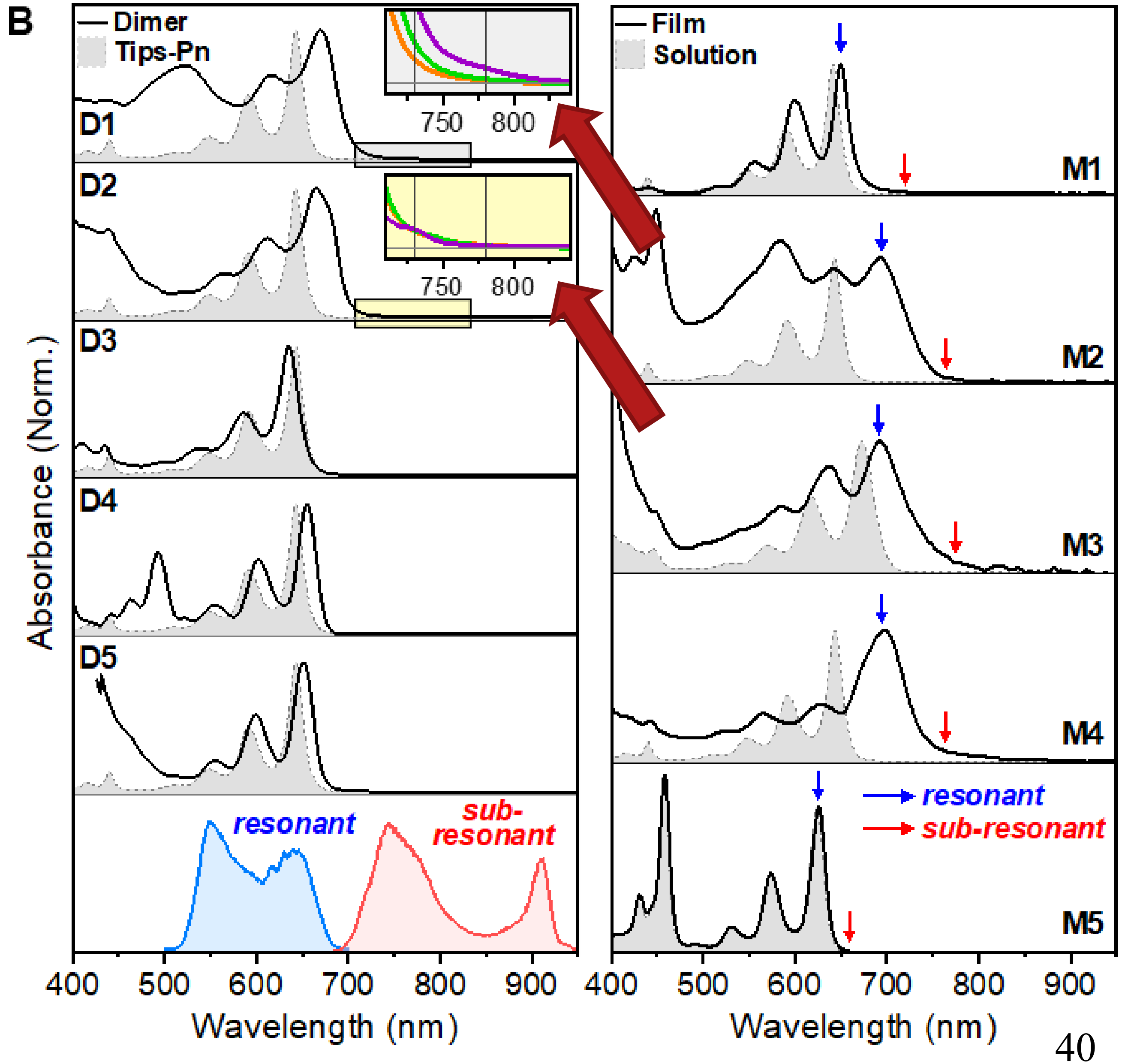
David G. Bossanyi[1], Maik Matthiesen[2], Shuangqing Wang[1], Joel A. Smith[1], Rachel C. Kilbride[1], James D. Shipp[3], Dimitri Chekulaev[3], Emma Holland[4], John E. Anthony[4], Jana Zaumseil[2], Andrew J. Musser[1,5] and Jenny Clark[1]

- ‘Dark’ ^{1}TT emits photons through a symmetry-breaking vibronic process
- What goes down must come up?

A zoo of pentacenes

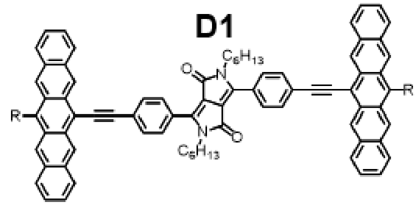
- Dimers in solution & monomers in thin film exhibit wide range of coupling strength (spectral shifts)

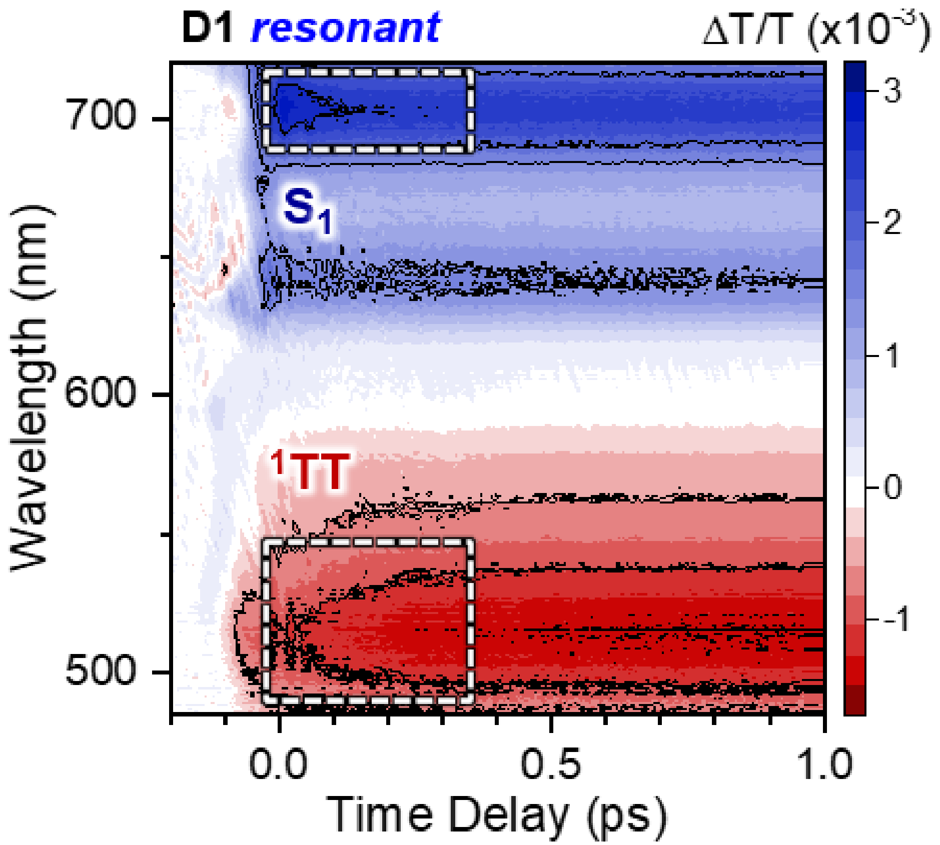


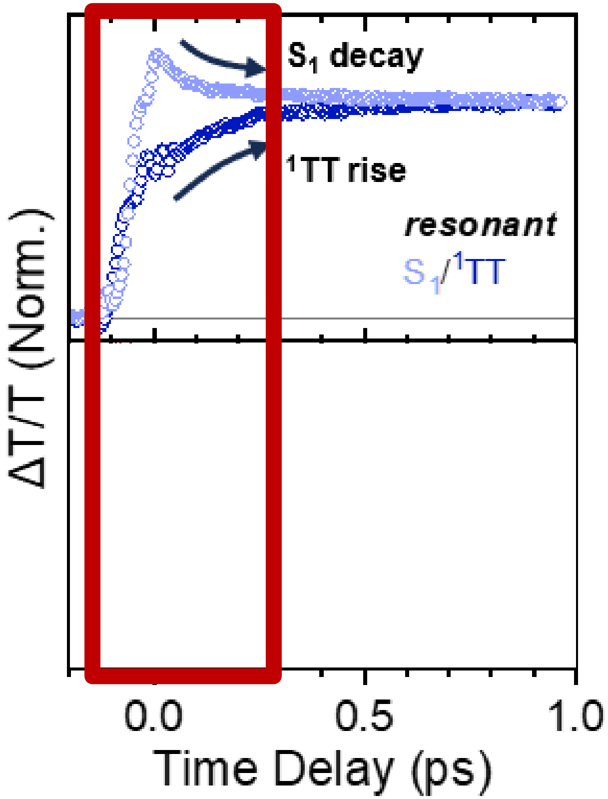


Kim, Bain et al., under review

Excitation-dependent SF dynamics



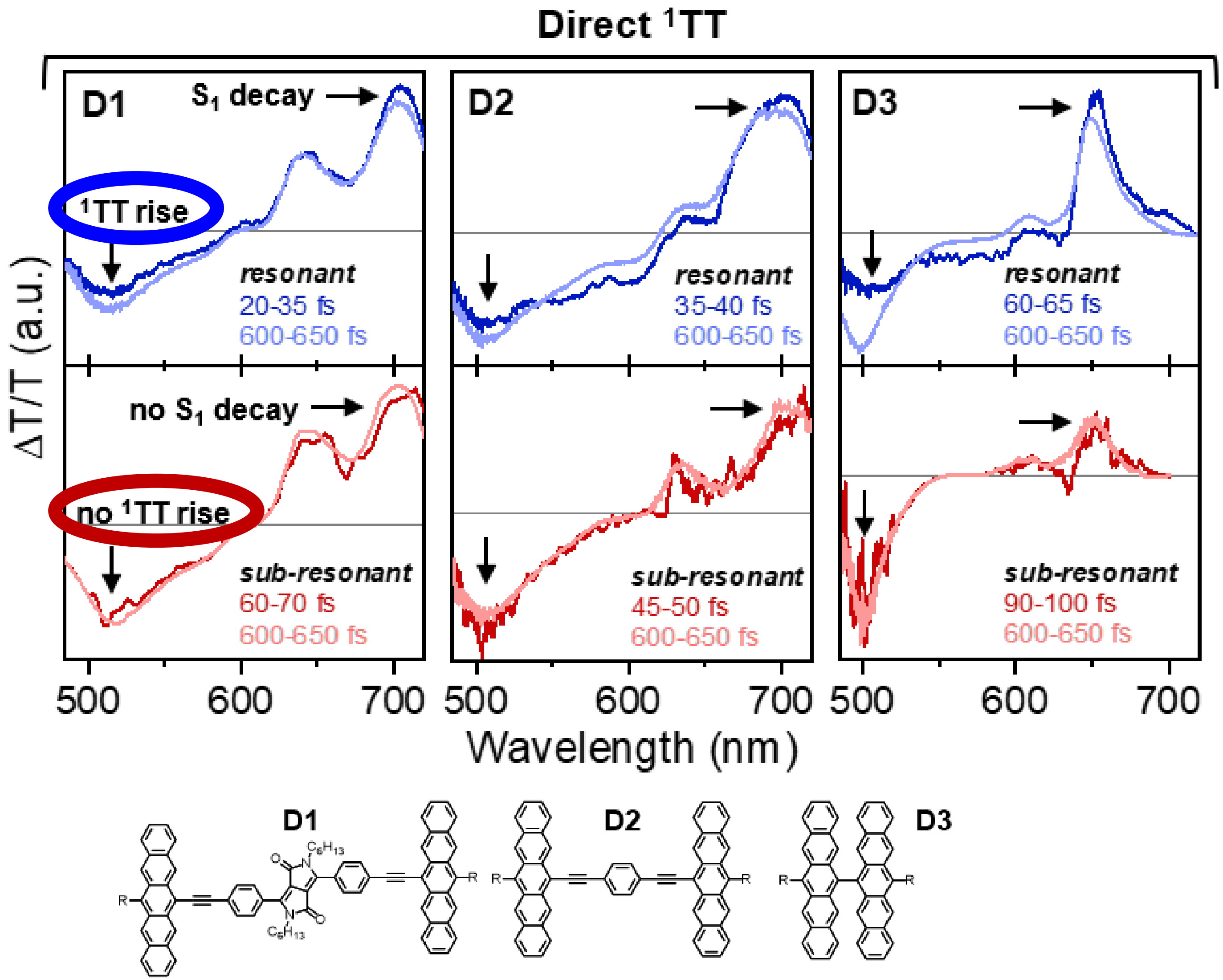


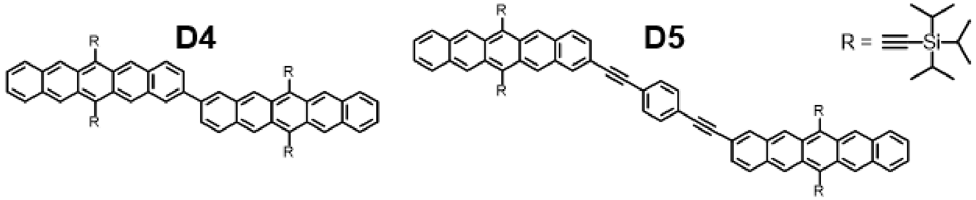


- Resonant: excite the S_1 absorption band
- Sub-resonant: excite ~where ^1TT should be

Kim, Bain et al., *under review*

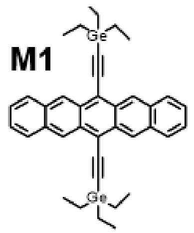
Direct excitation of ^{1}TT in dimers

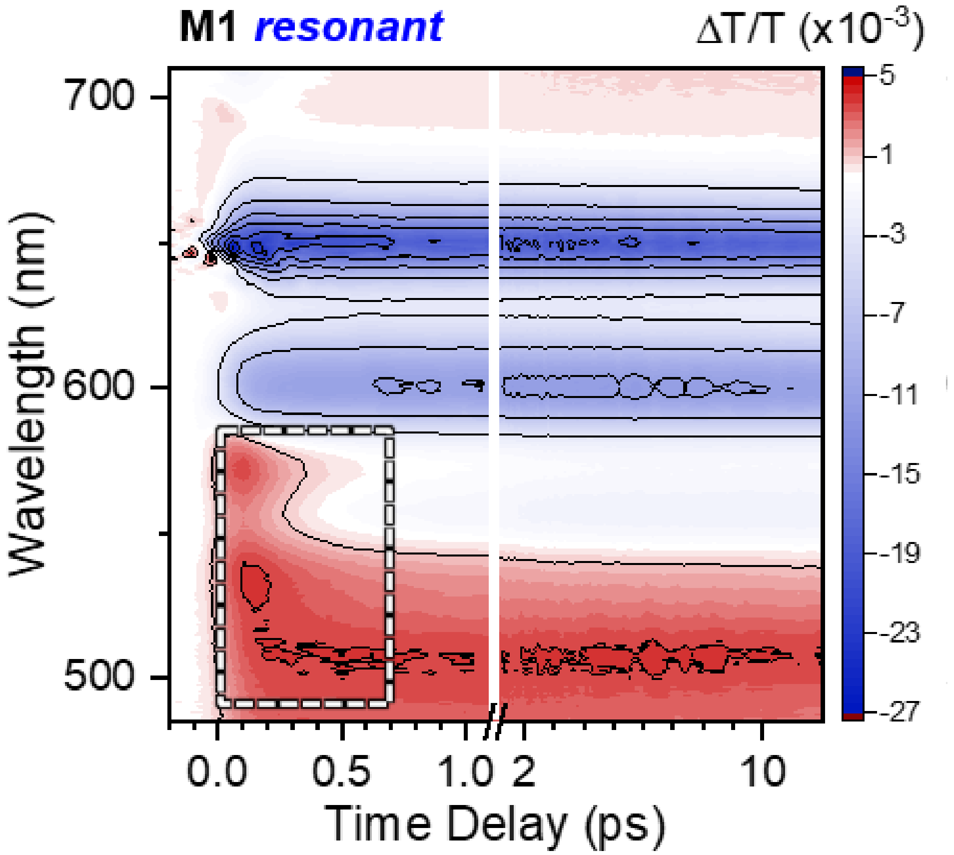


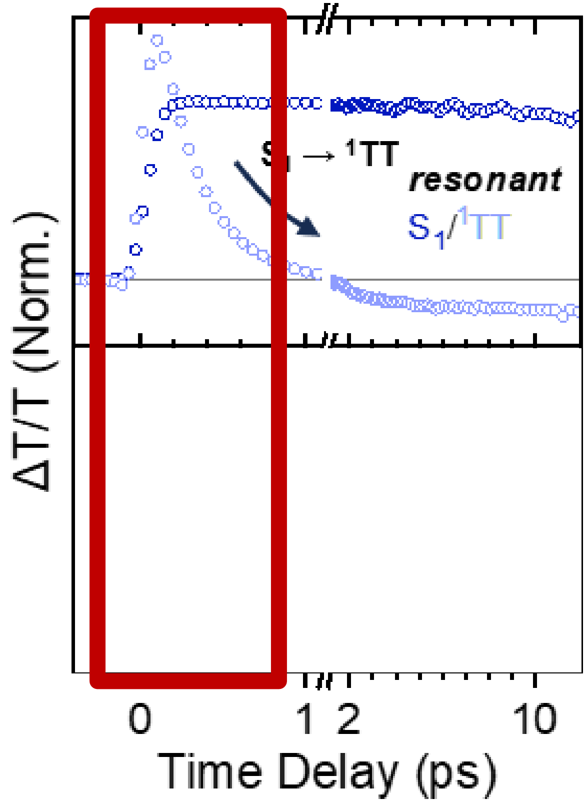


Kim, Bain et al., under review

Excitation-dependent SF dynamics in films







- Resonant: excite the S_1 absorption band
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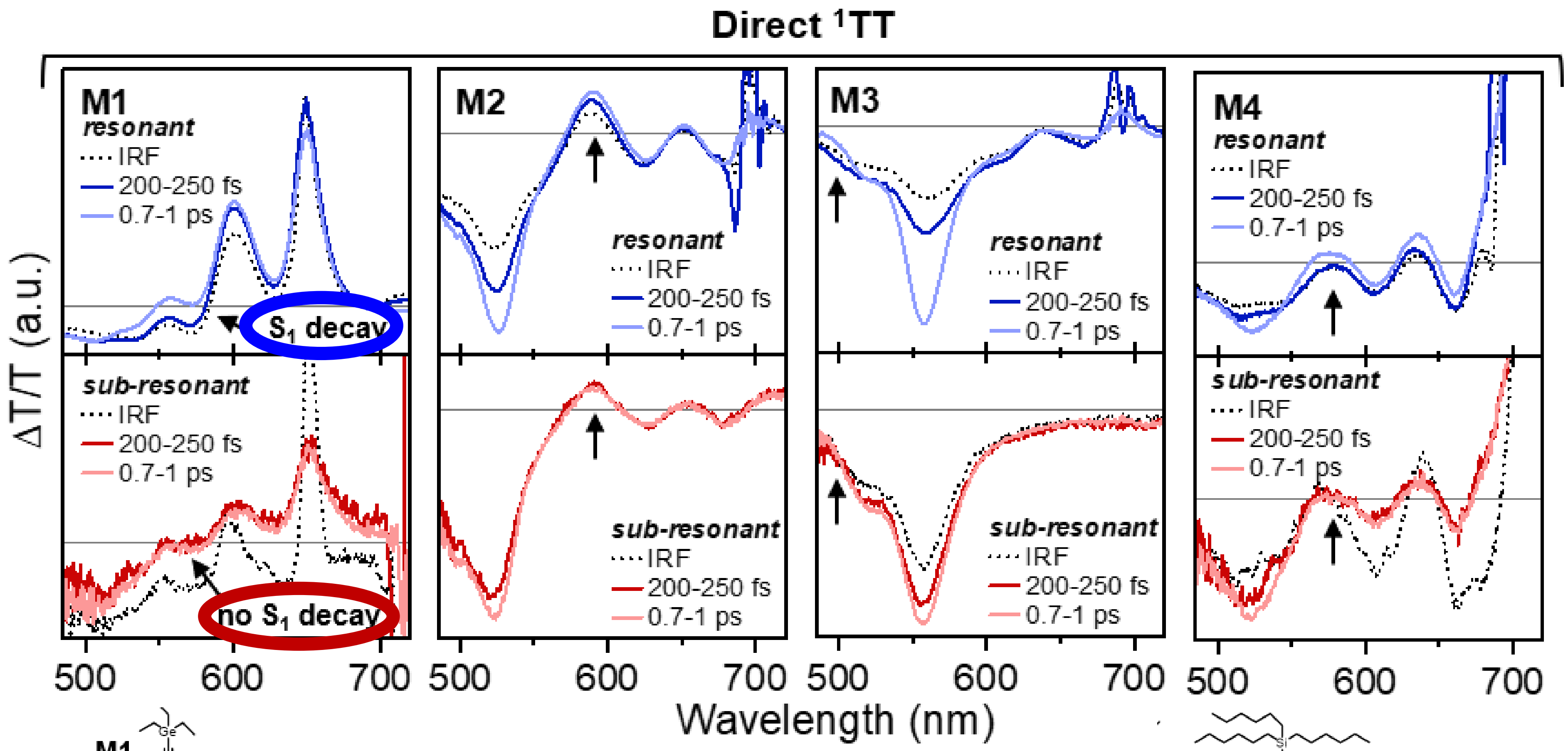
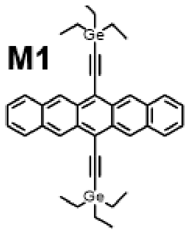
Kim, Bain et al., under review

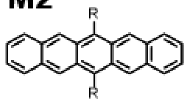
Direct excitation of ^{1}TT in films



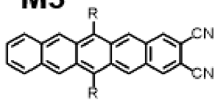
M1



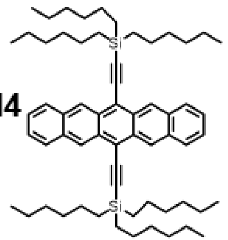
M2



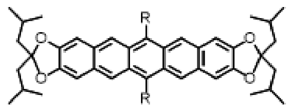
M3



M4



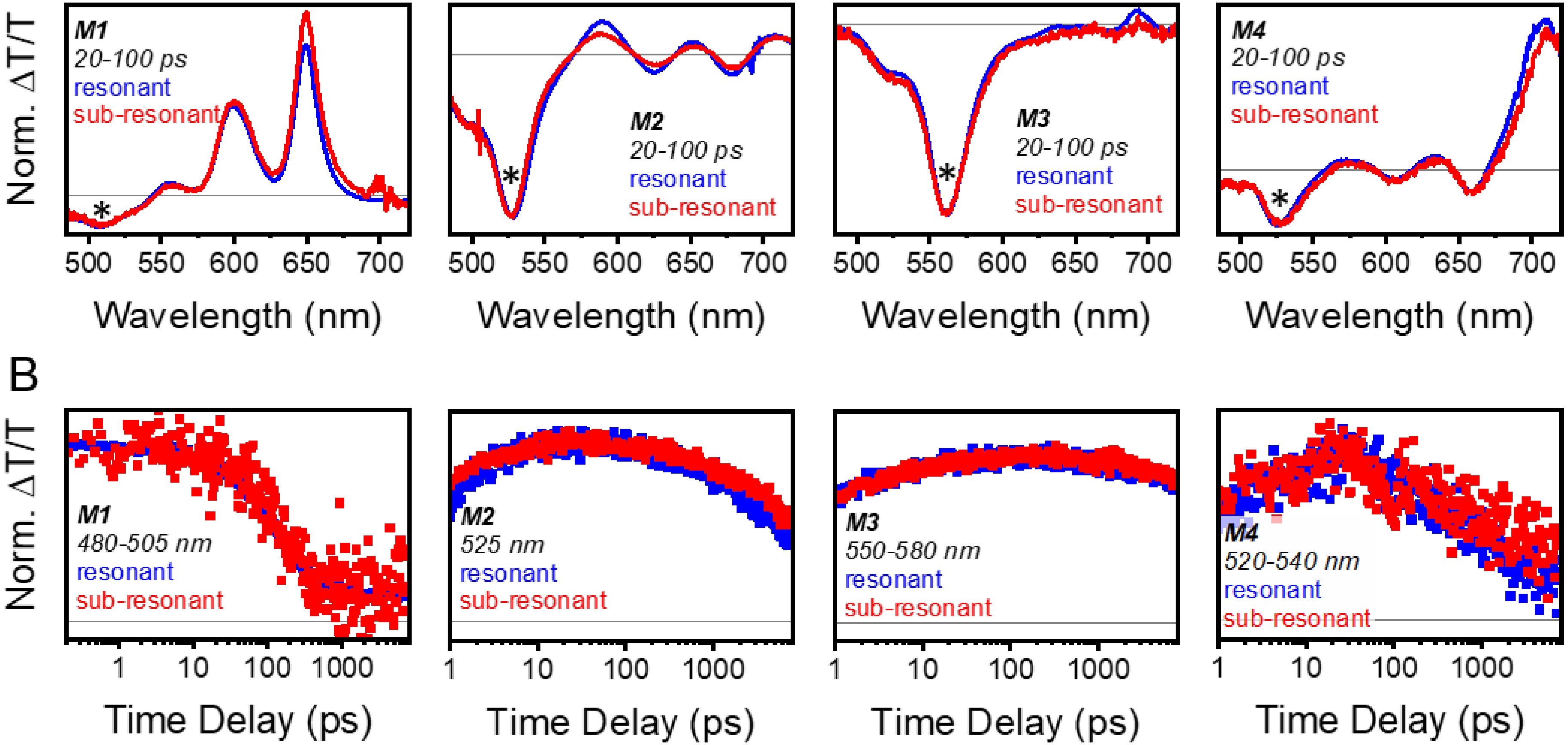
M5



Kim, Bain et al., under review

All roads lead to T+T

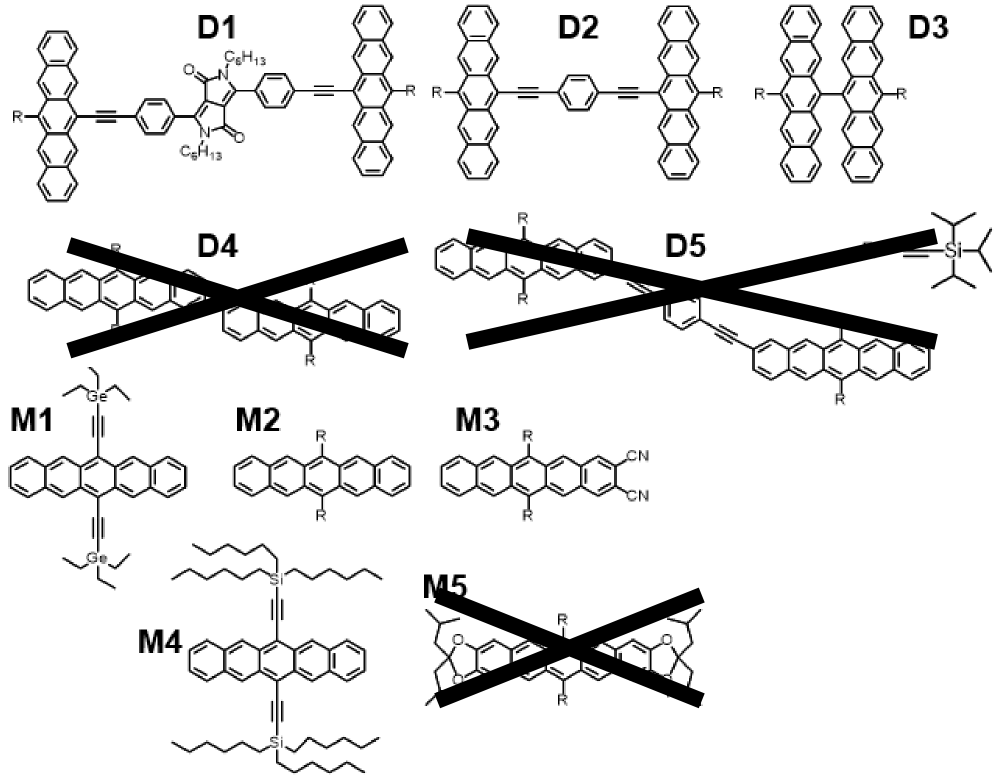
- Identical decay pathway once ^{1}TT is formed, regardless of how we produce it

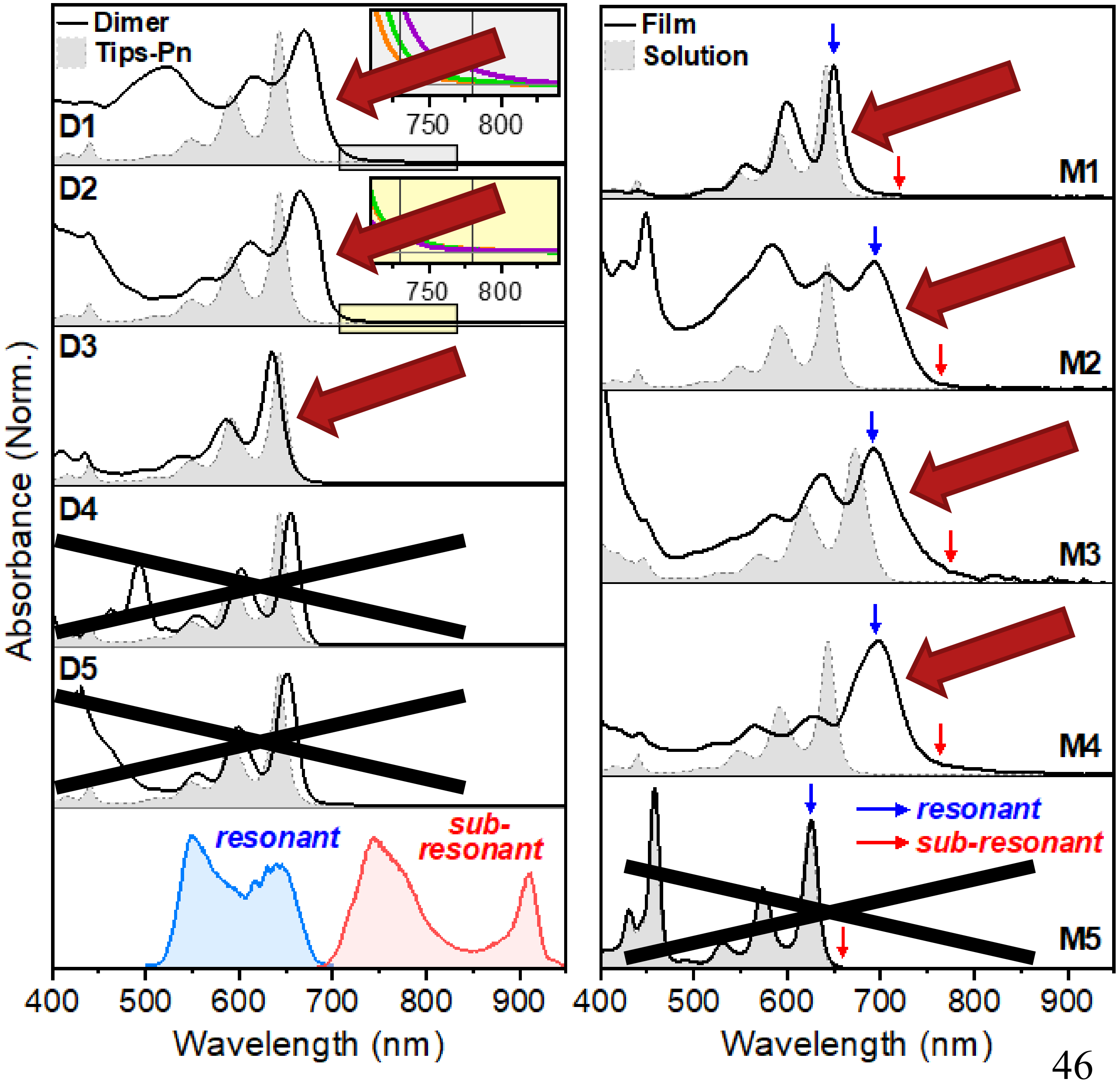


Kim, Bain et al., under review

Molecules matter

- All ‘strongly interacting’ pentacenes enable direct excitation of ^{1}TT
- Role for delocalization

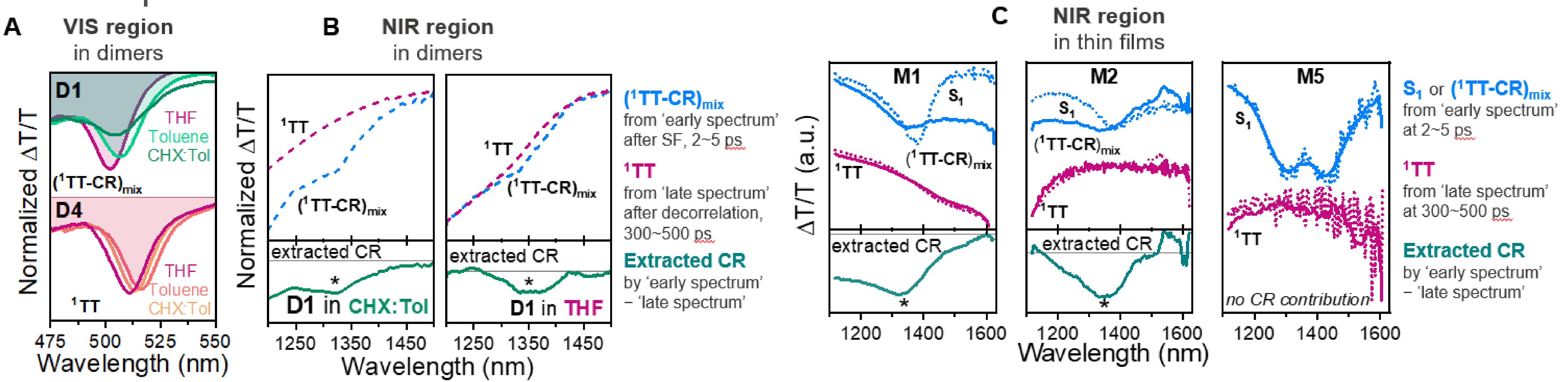




Kim, Bain et al., under review

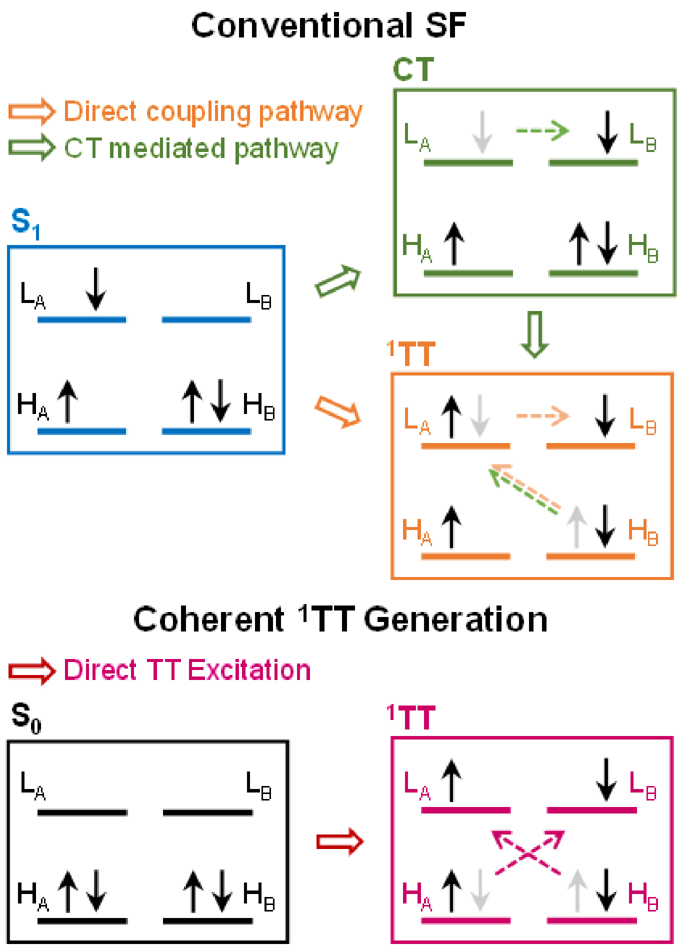
Charge resonance character

- Signatures of CR-state mixing into 1TT wavefunction:
  - Broadening & weakening of TT absorption in visible
  - Appearance of new cation-linked peak in NIR
- CR signatures correlate with ability to directly excite TT & vanish during separation

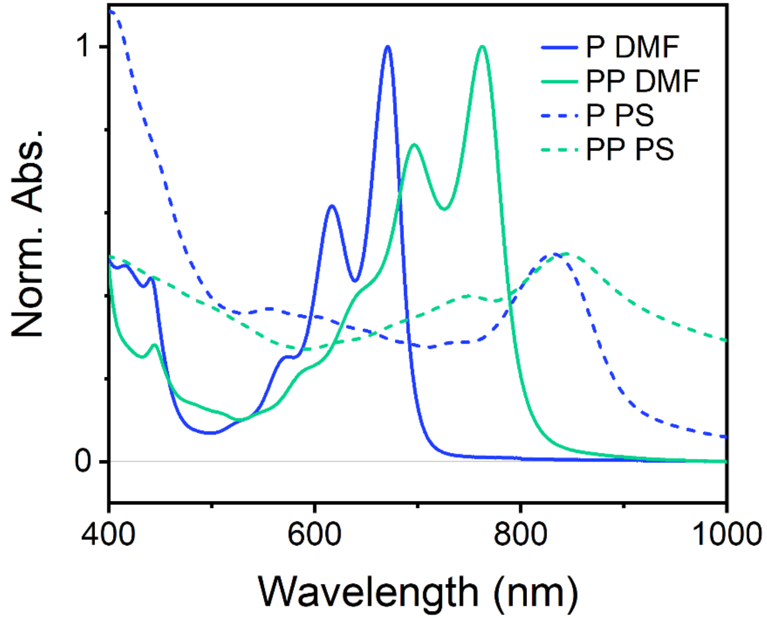


Kim, Bain et al., under review

A recipe for coherent ^{1}TT excitation?

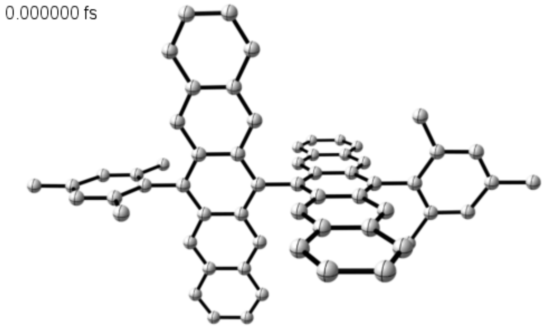


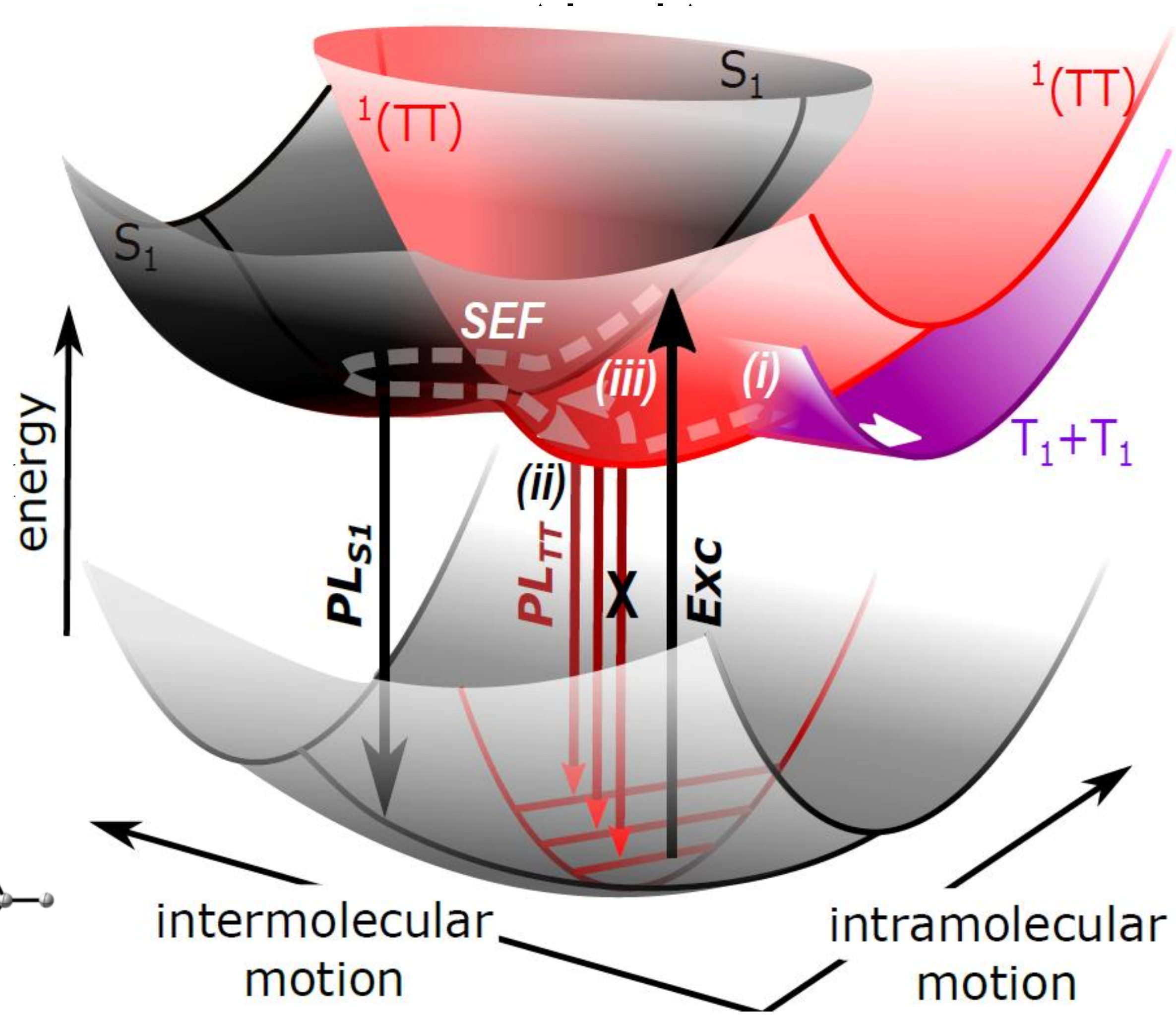
- Design Pc side groups to steer packing and maximize orbital overlap for CR coupling
- Extreme absorbance shift in self-assembled aggregates in solution
- Mixed ^{1}TT becomes the primary excited state?



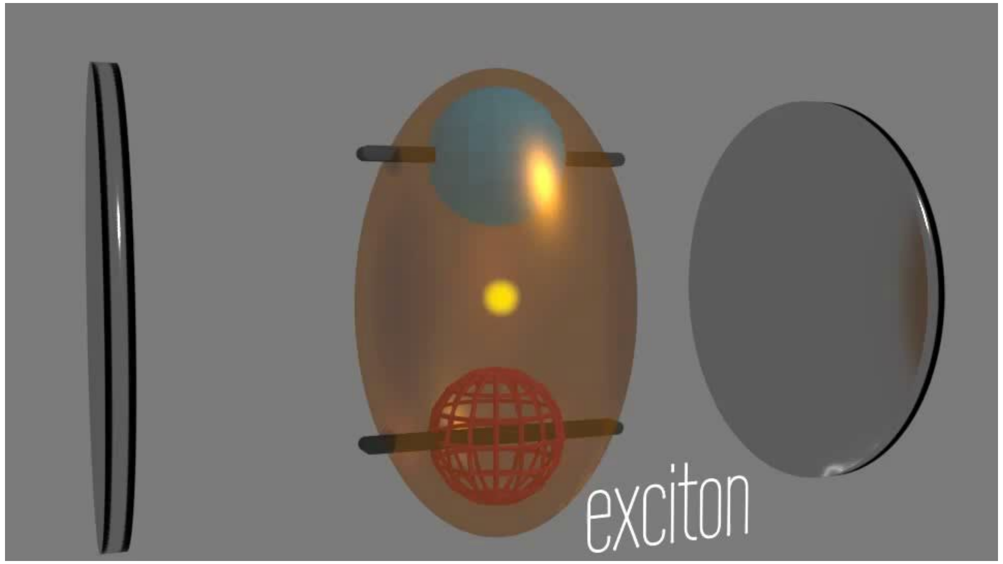
Beyond bright & dark

- Simple pictures of organic photophysics are appealing…
- Vibronic coupling & disorder cause states to mix & behave in unexpected ways
- **Complexity yields opportunity**





Molecules are messy



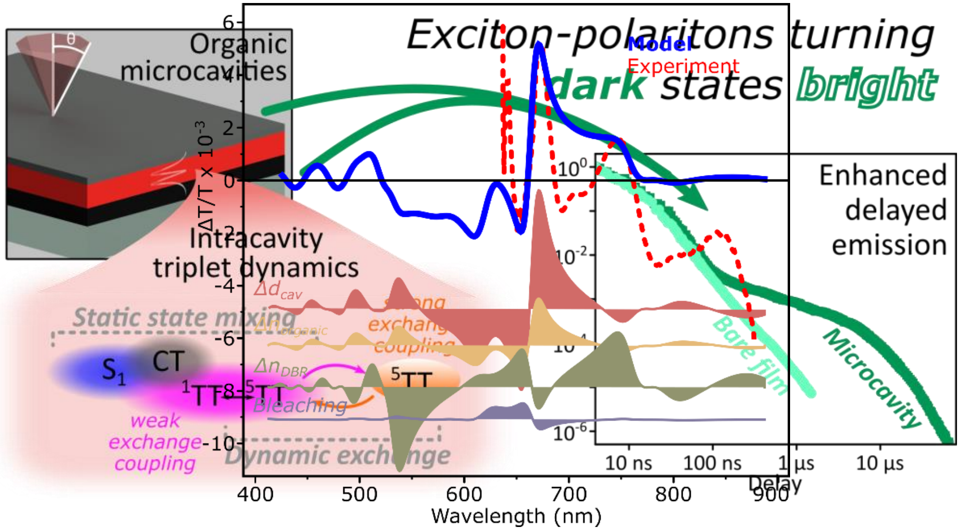
- Exquisitely sensitive to artefacts
- Not just about the bright states, even when they do something interesting!
- Molecular dark states & disorder cannot be ignored
-

Chem CellPress

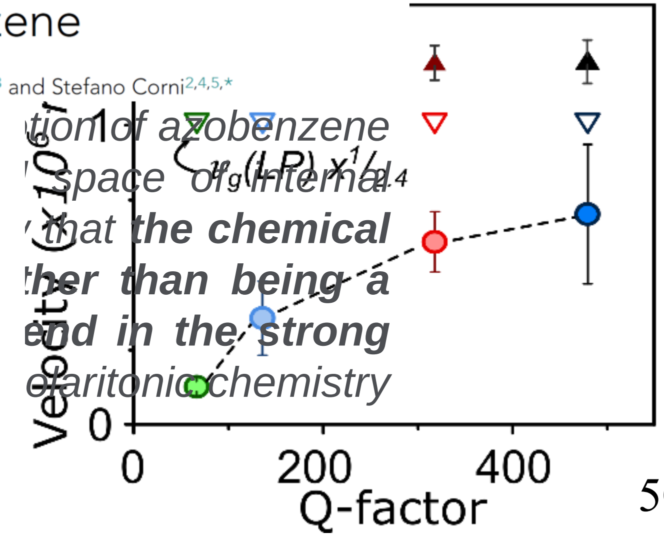
Article

Strong Coupling with Light Enhances the Photoisomerization Quantum Yield of Azobenzene

Jacopo Fregoni,[1,2] Giovanni Granucci,[3,*] Maurizio Persico,[3] and Stefano Corni[2,4,5,*]



Polak *et al.*, Chem Sci 2020
Renken *et al.*, J Chem Phys 2021
Pandya *et al.*, Adv Sci 2022
Khazanov *et al.*, Chem Phys Rev 2023
George *et al.*, arXiv: 2309.13178



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Alfred P. Sloan Foundation
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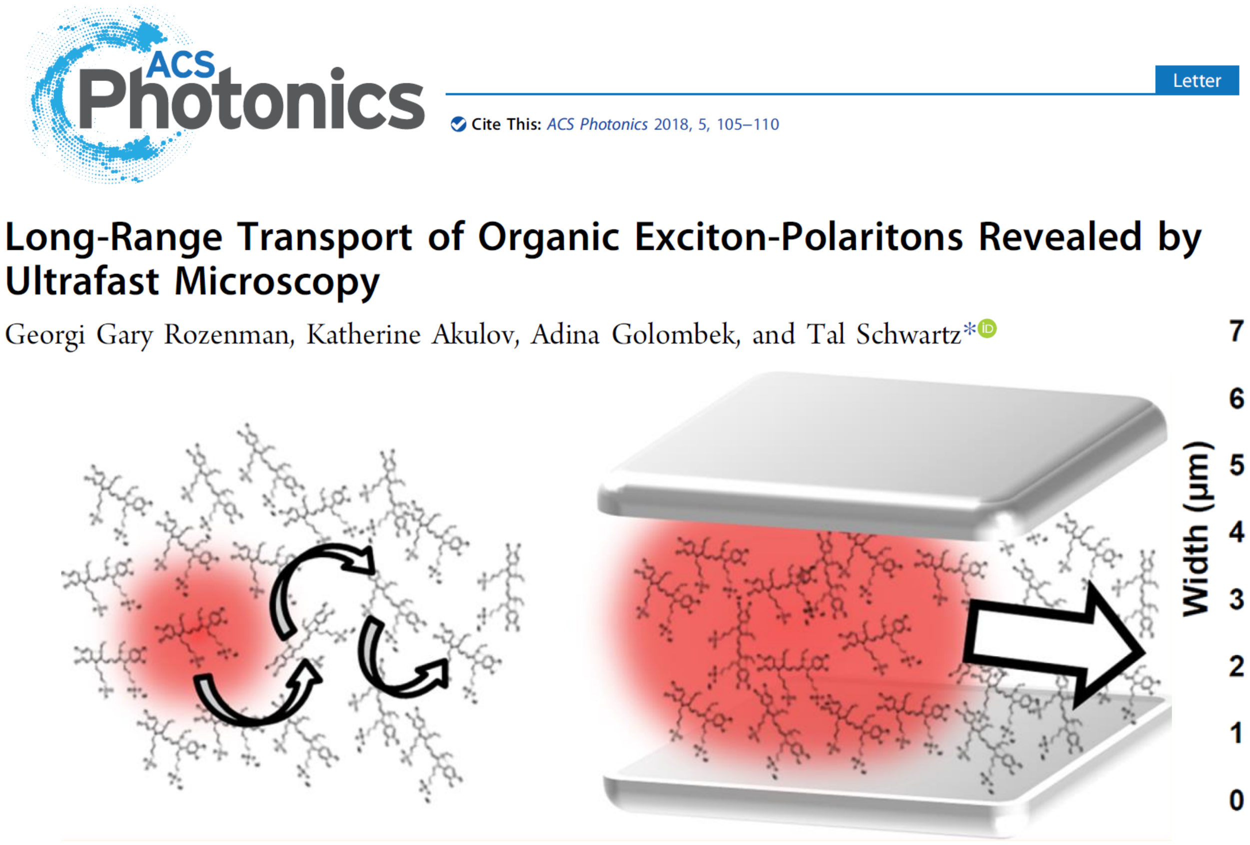
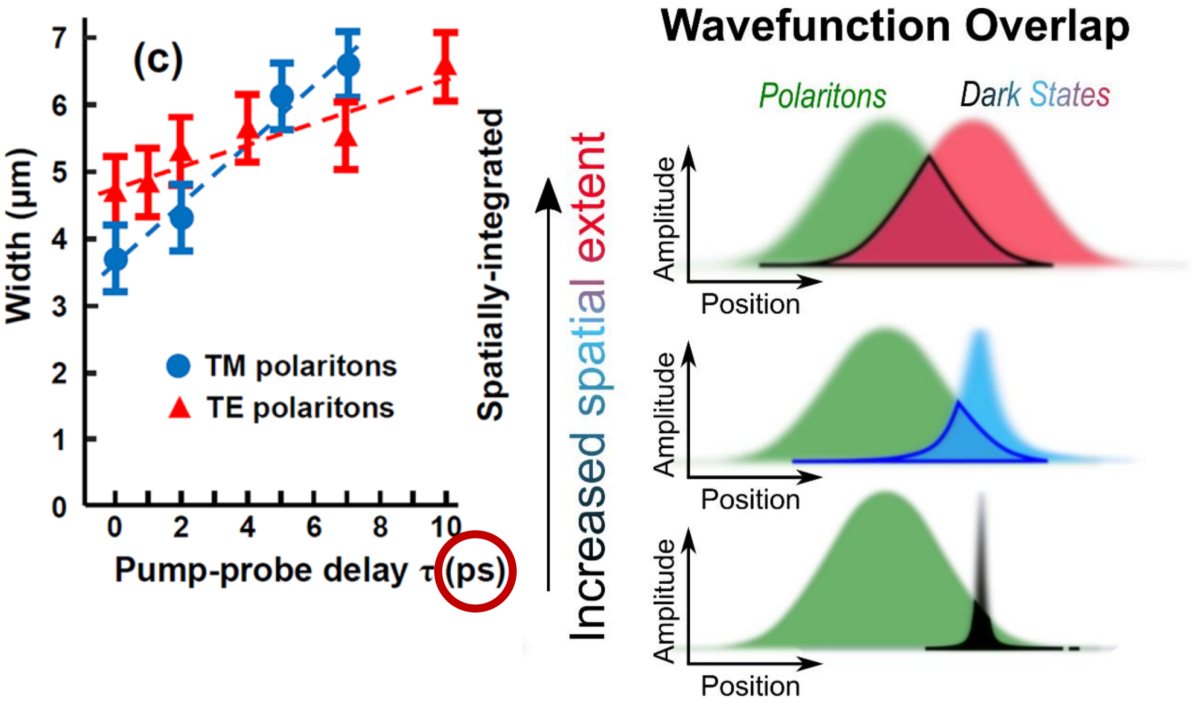
Condensed Phase and Interfacial Molecular Science (CPIMS)
Chemical Sciences, Biosciences, and Geosciences Division
NSF

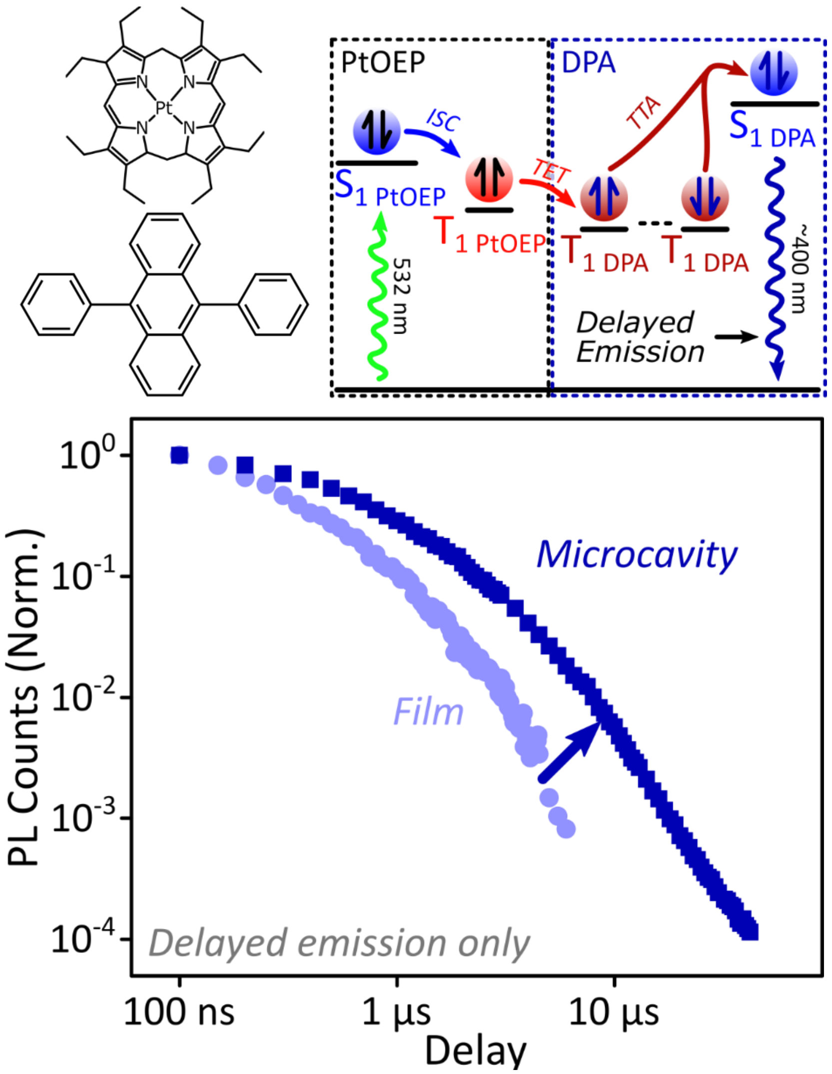
Different flavors of delocalization?

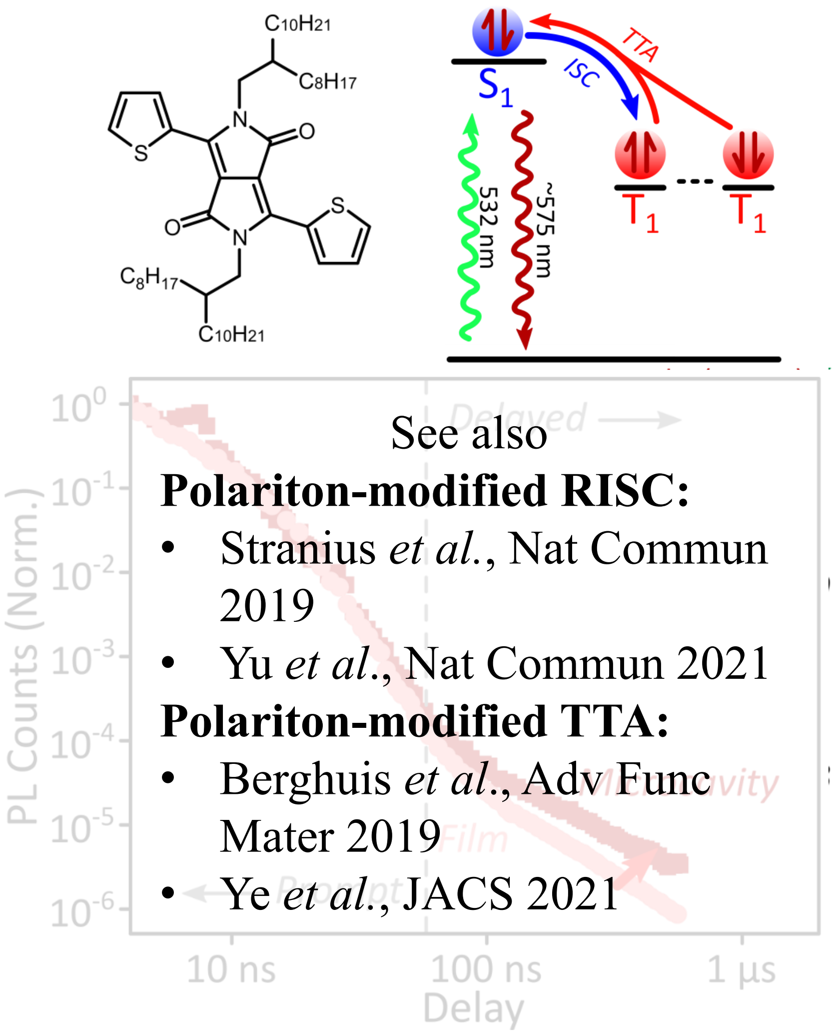




Pandya… Musser, Advanced Science 2022

Not just the bright states: TT ‘harvesting’





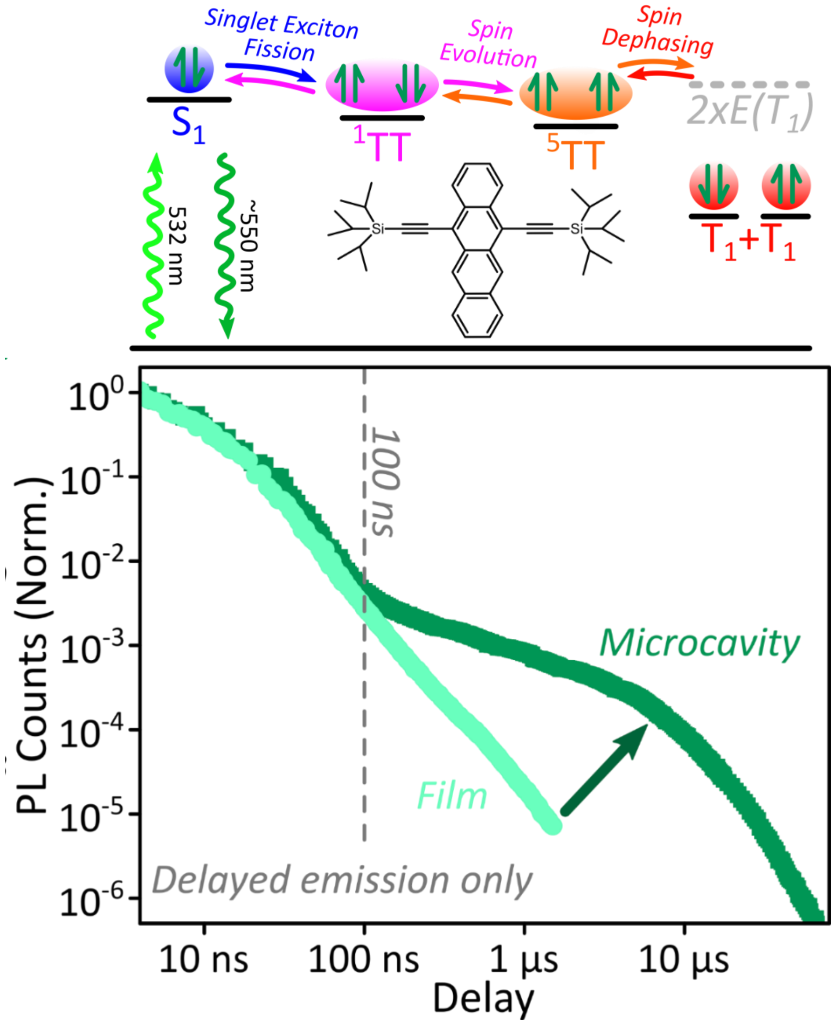
See also

Polariton-modified RISC:

- Stranius *et al.*, Nat Commun 2019
- Yu *et al.*, Nat Commun 2021

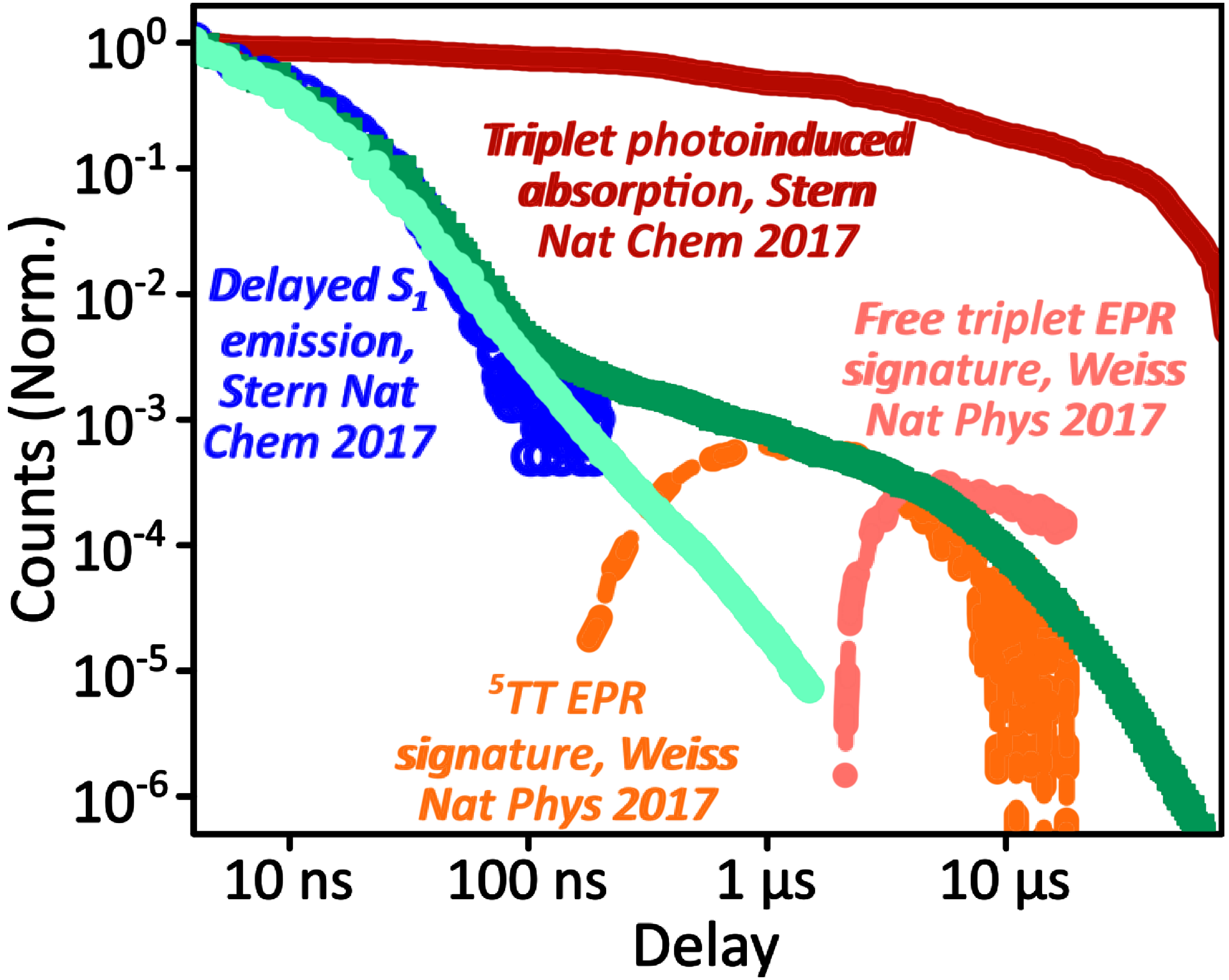
Polariton-modified TTA:

- Berghuis *et al.*, Adv Func Mater 2019
- Ye *et al.*, JACS 2021



Polak… Musser, Chem Sci 2020

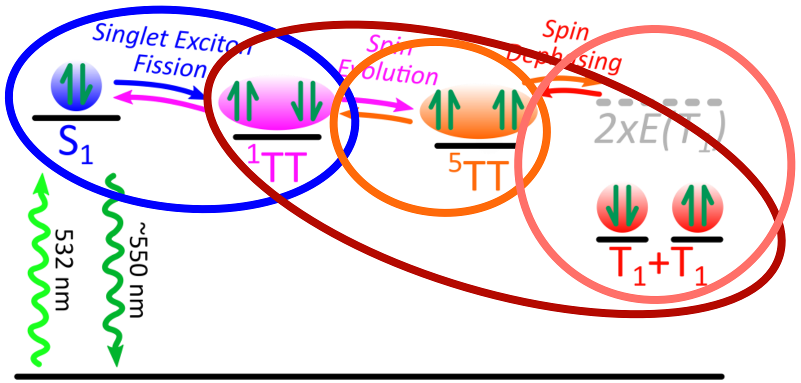
Into the black (silver?) box



nature chemistry ARTICLES
PUBLISHED ONLINE: 11 SEPTEMBER 2017 | DOI: 10.1038/NCHEM.2856

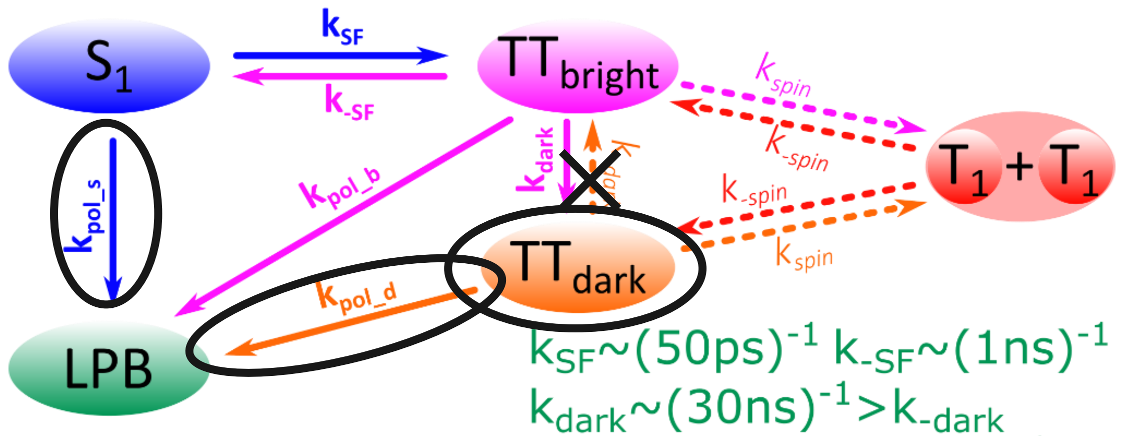
Vibronically coherent ultrafast triplet-pair formation and subsequent thermally activated dissociation control efficient endothermic singlet fission

Hannah L. Stern[1], Alexandre Cheminal[1], Shane R. Yost[2,3], Katharina Broch[1], Sam L. Bayliss[1], Kai Chen[4,5], Maxim Tabachnyk[1], Karl Thorley[6], Neil Greenham[1], Justin M. Hodgkiss[4,5], John Anthony[6], Martin Head-Gordon[2,3], Andrew J. Musser[1,7], Akshay Rao[1*] and Richard H. Friend[1*]



Polak… Musser, Chem Sci 2020

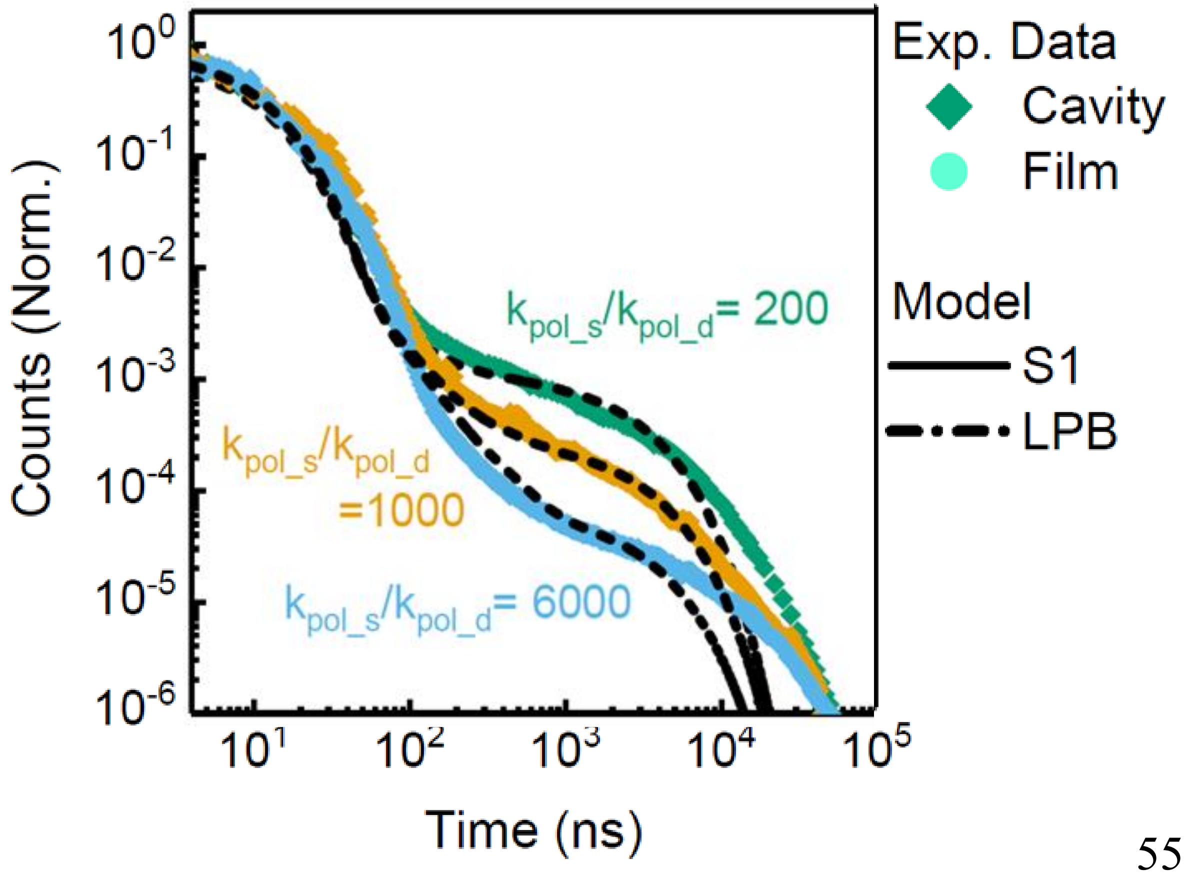
Quintet 'harvesting'? Rate model



TIPS-tetracene: k_{SF}~(50ps)$^{-1}$ k_{-SF}~(1ns)$^{-1}$
k_{dark}~(30ns)$^{-1}$>k_{-dark}
k_{pol_s}~k_{pol_b}<(100ns)$^{-1}$
k_{pol_d}~0.005*k_{pol_s}
k_{spin}~(10μs)$^{-1}$

- Scattering of bright states into LPB strictly limited → population dynamics remain similar to film
- Polariton enhancement best fit with k_{pol_d}>0

- Bulk of population resides in pool of high-spin TT_{dark}



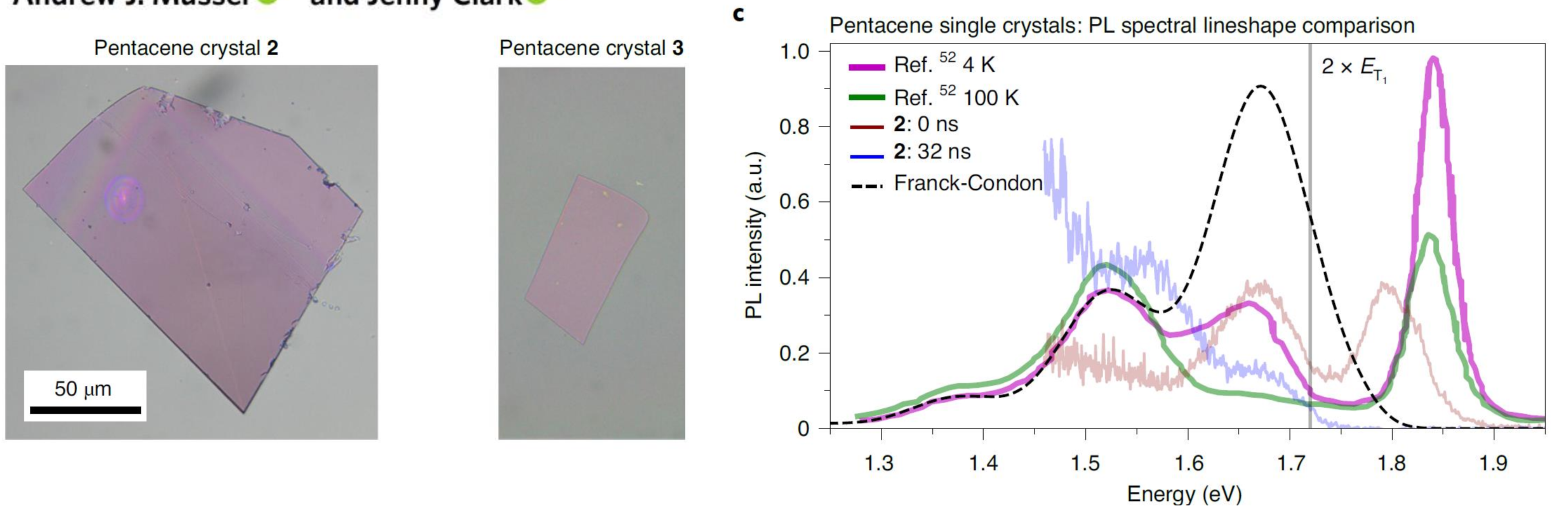
Polak… Musser, Chem Sci 2020

Truly dark?

nature chemistry
ARTICLES
https://doi.org/10.1038/s41557-020-00593-y
Check for updates

Emissive spin-0 triplet-pairs are a direct product of triplet–triplet annihilation in pentacene single crystals and anthradithiophene films

David G. Bossanyi[1]✉, Maik Matthiesen[2], Shuangqing Wang[1], Joel A. Smith[1], Rachel C. Kilbride[1], James D. Shipp[3], Dimitri Chekulaev[3], Emma Holland[4], John E. Anthony[4], Jana Zaumseil[2], Andrew J. Musser[1,5] and Jenny Clark[1]✉

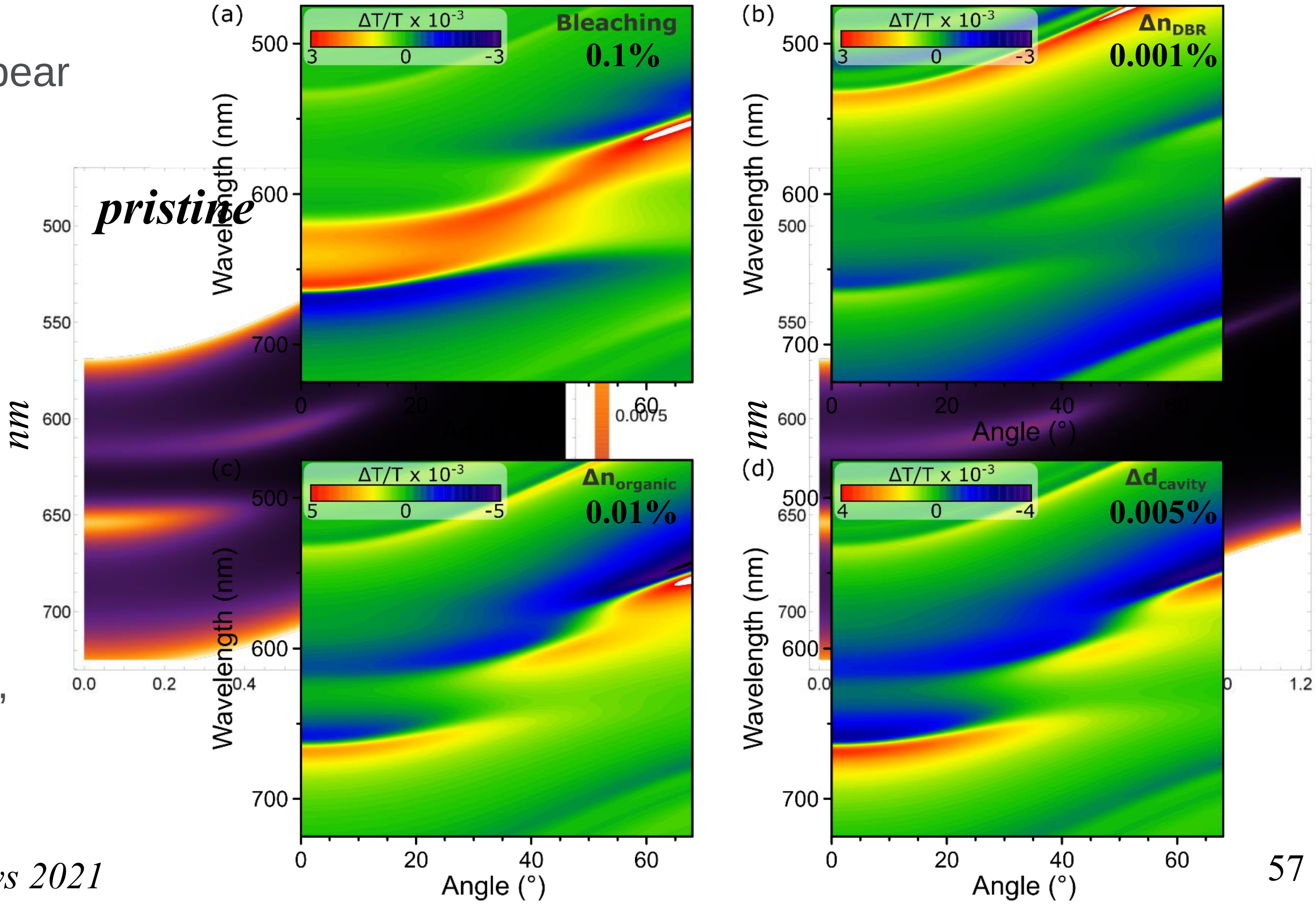


- Mixing with S_1, CT stabilizes ^1TT
- Results in rapid, long-range transport
- Herzberg-Teller coupling enables symmetry-forbidden direct ^1TT emission
- … so is it ‘just’ emitting in the microcavity?

See also: Musser & Clark, Annu Rev Phys Chem 2019

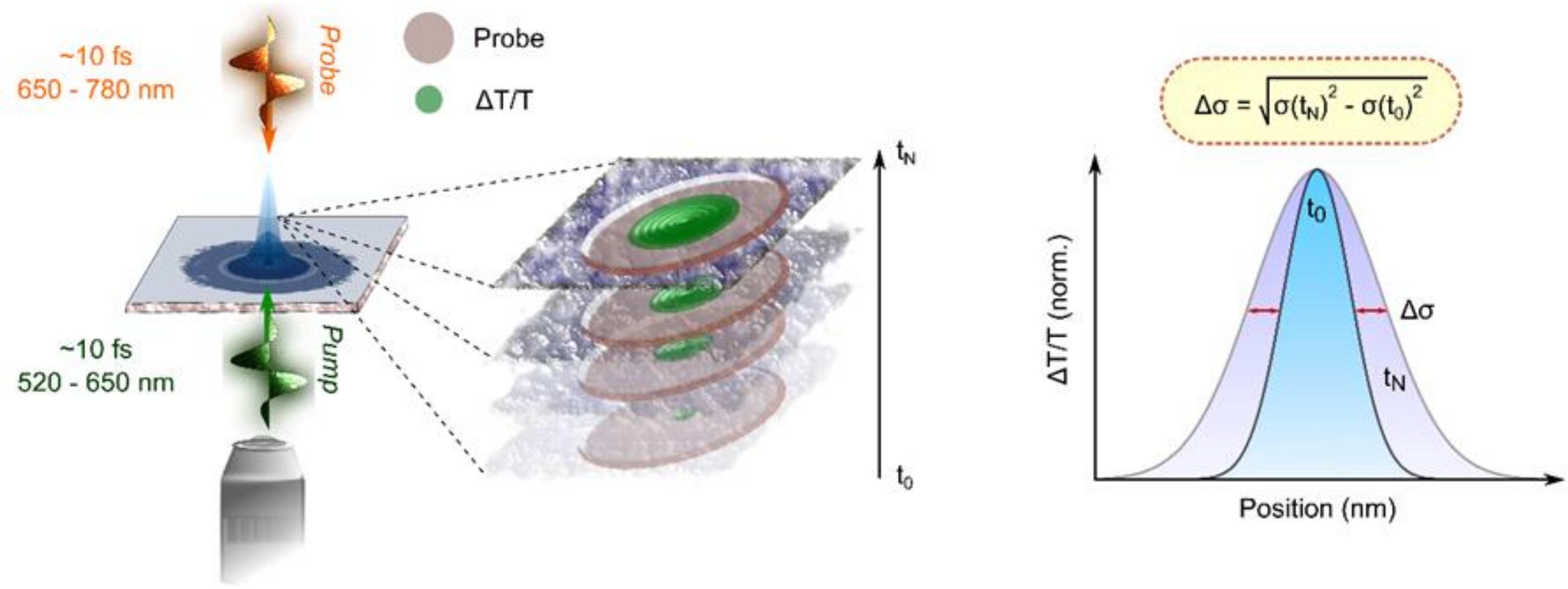
Simulating cavity excitation effects 2

- Calculated dispersions appear identical to pristine cavity
- Model TA signal as
  $$\frac{\Delta T}{T} = \frac{T_{sim\ ON} - T_{sim\ OFF}}{T_{sim\ OFF}}$$
- Extremely small changes yield TA signatures of observed magnitude
- Each governed by intrinsic, typically slow dynamics



Renken, Pandya… Musser, J Chem Phys 2021

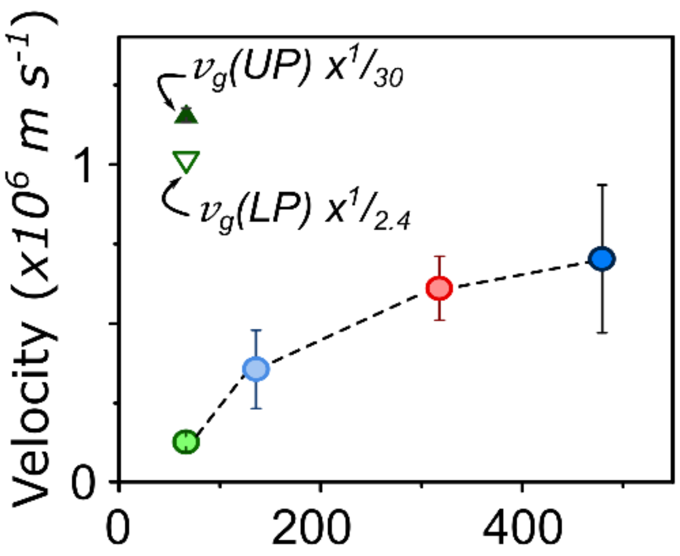
Polariton transport with 10-fs TAM

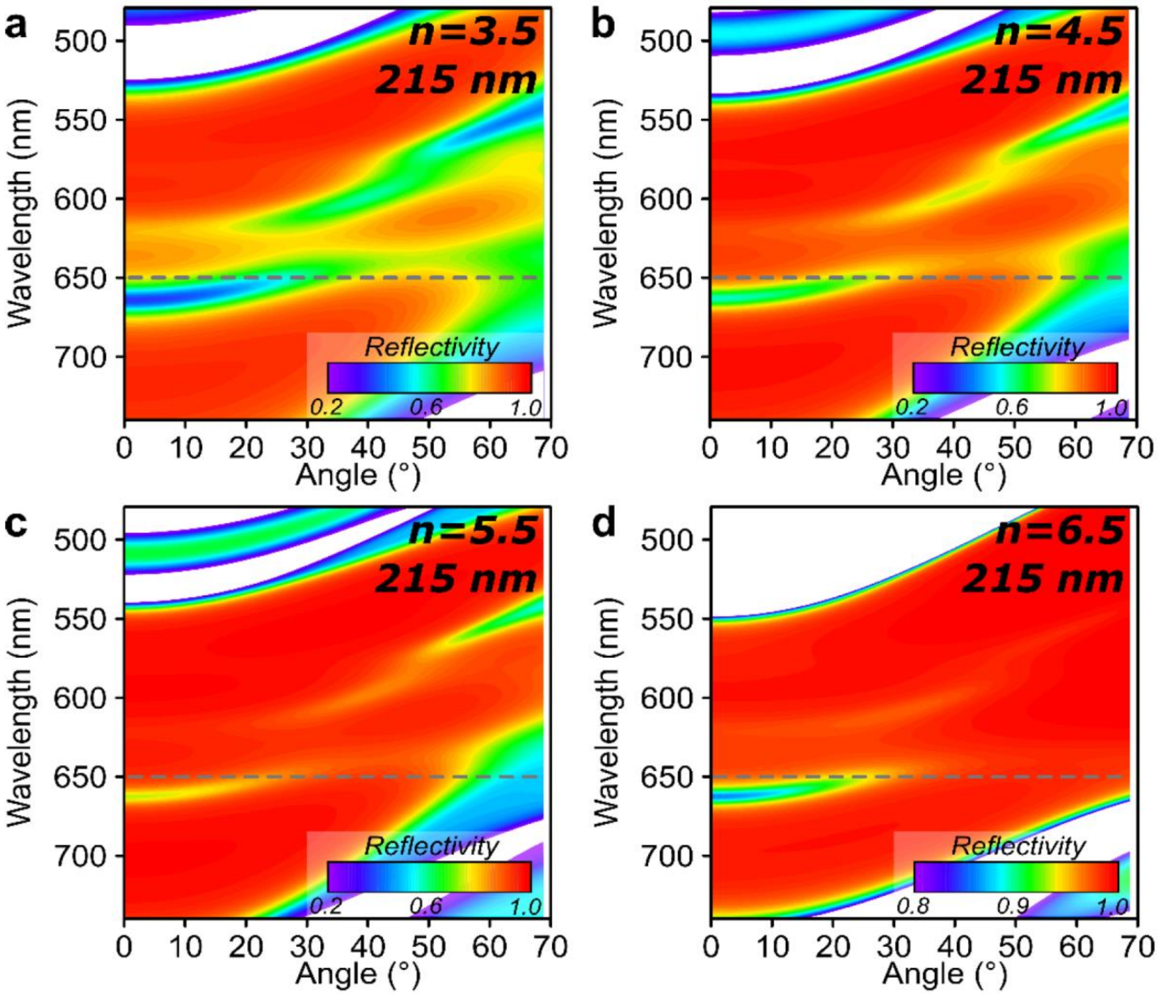


Pandya… Musser, Advanced Science 2022

Q-dependence?

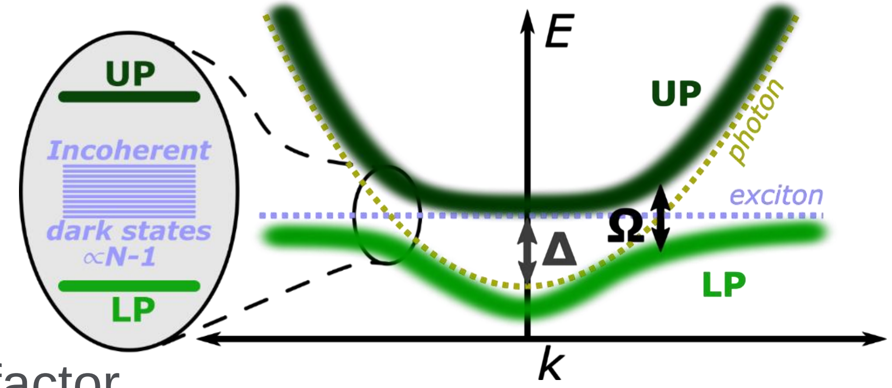
- Photonic lifetime increases with improved confinement
- Photonic vs excitonic character *does not change* with increasing Q-factor
- Dispersion *does not change* with increasing Q-factor





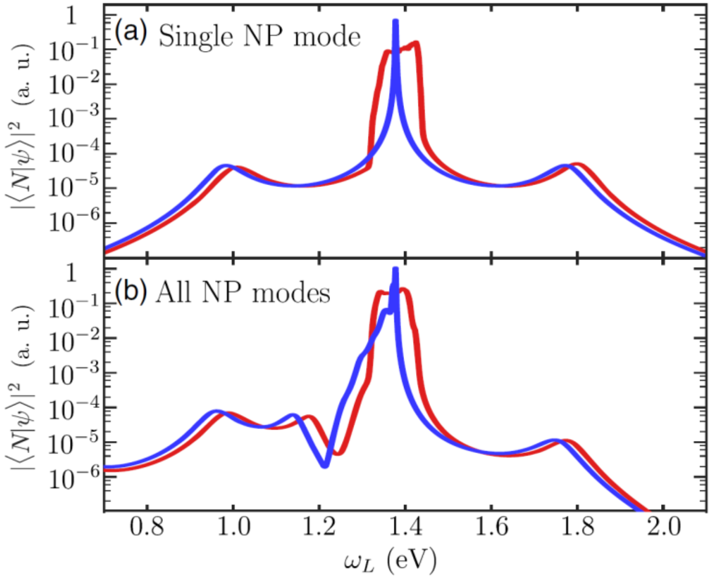
Pandya… Musser, Advanced Science 2022

The polaritons are not alone

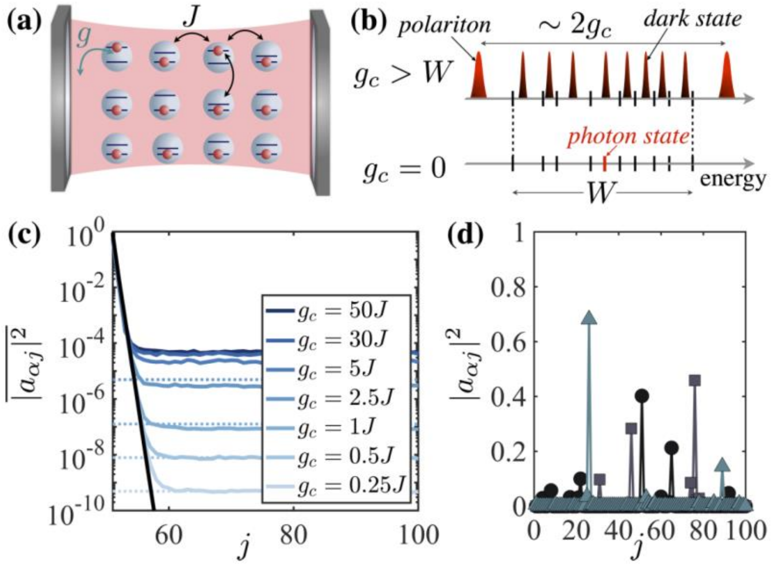


- Polariton states should be unaffected by cavity quality
- Coexist with less popular ‘dark’ intracavity states
- Models suggest these can be delocalized with increasing Q-factor

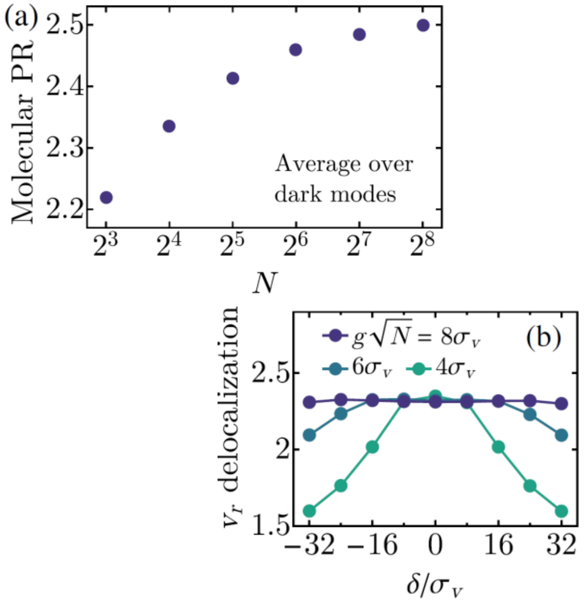
Gonzalez-Ballestero *et al.*, *PRL* 2016



Botzung *et al.*, *PRB* 2020



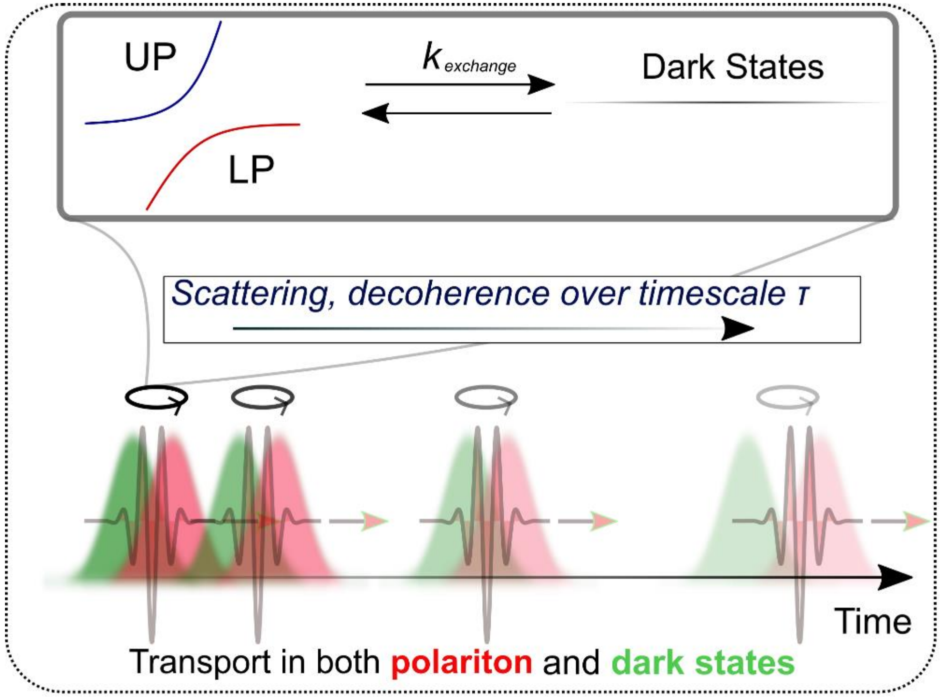
Du & Yuen-Zhou, *PRL* 2022

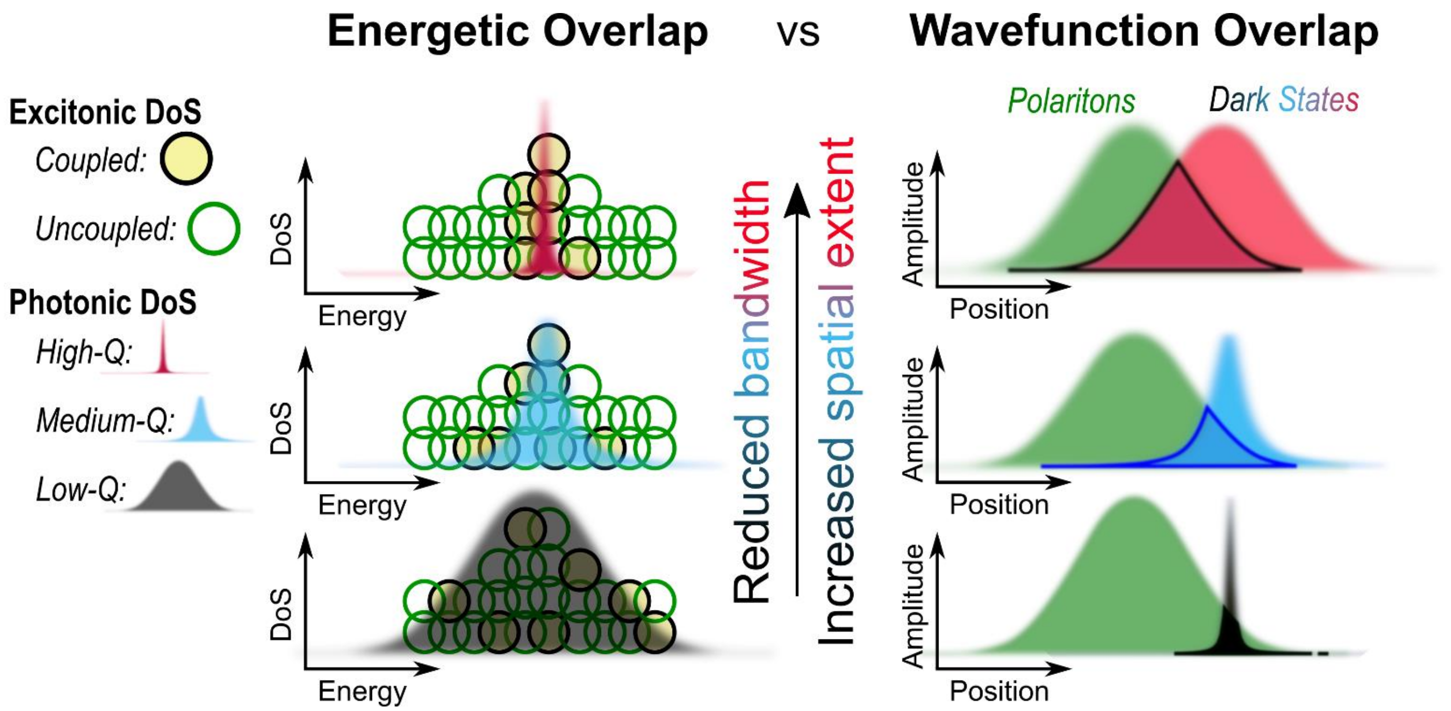


Pandya… Musser, Advanced Science 2022

Model of Q-factor control

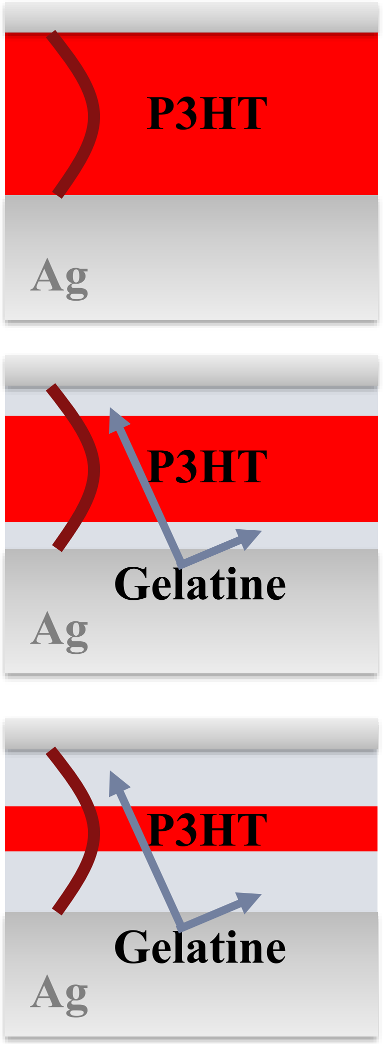
- Ballistic transport from polaritons, and Q-factor sensitivity from dark states
- Demands exceptionally rapid interplay between the bright and dark states
  - Both a brake and reservoir for longer-lived transport

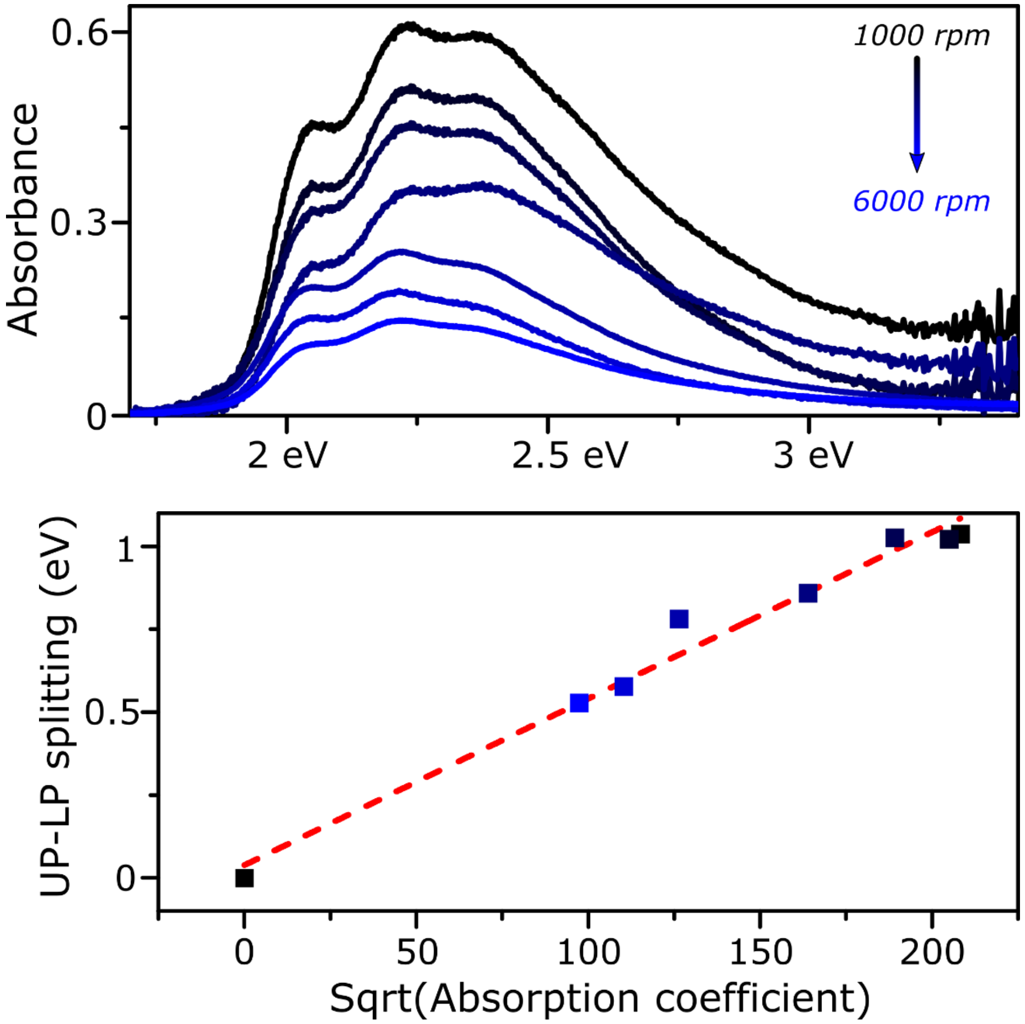


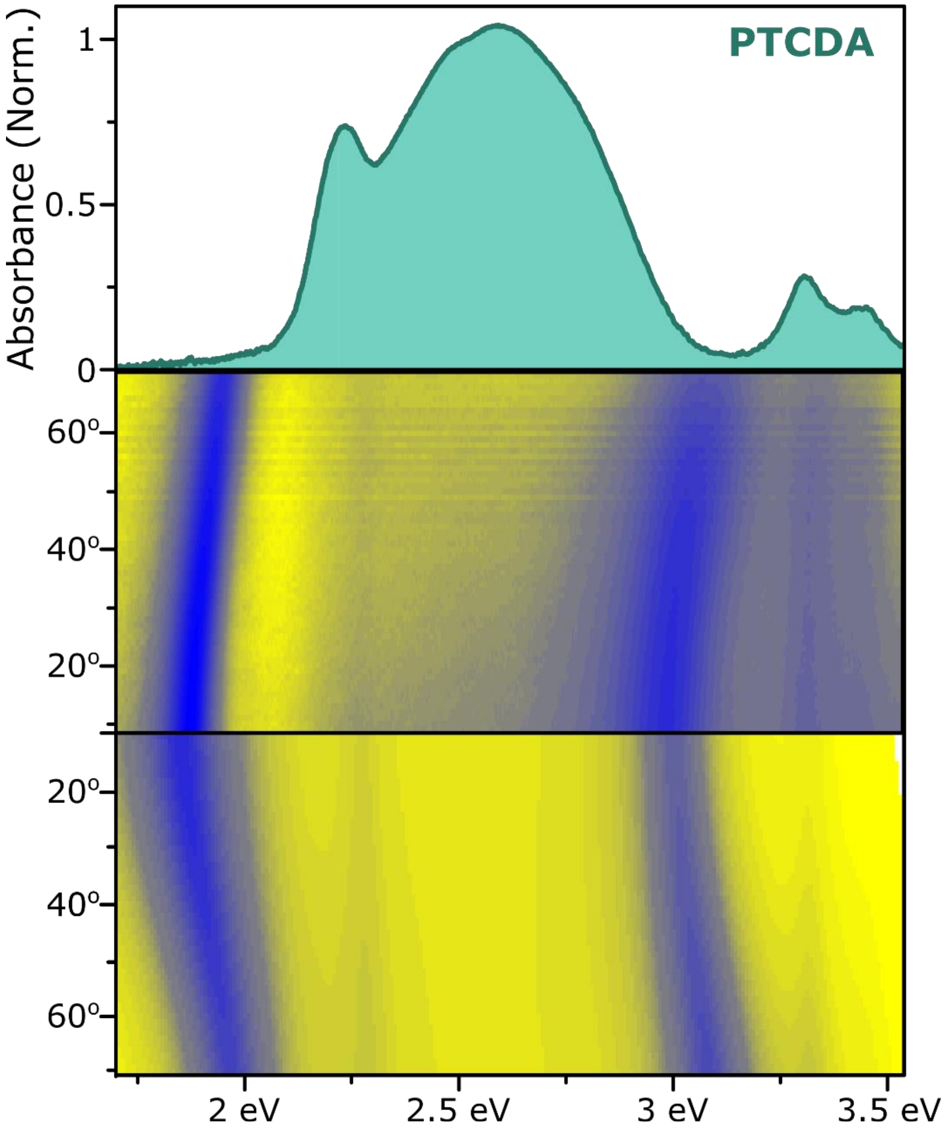


Pandya… Musser, Advanced Science 2022

‘Concentration’ dependence

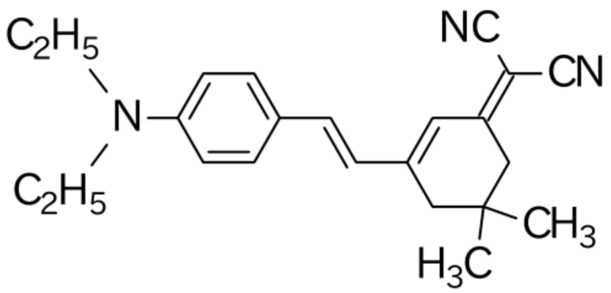




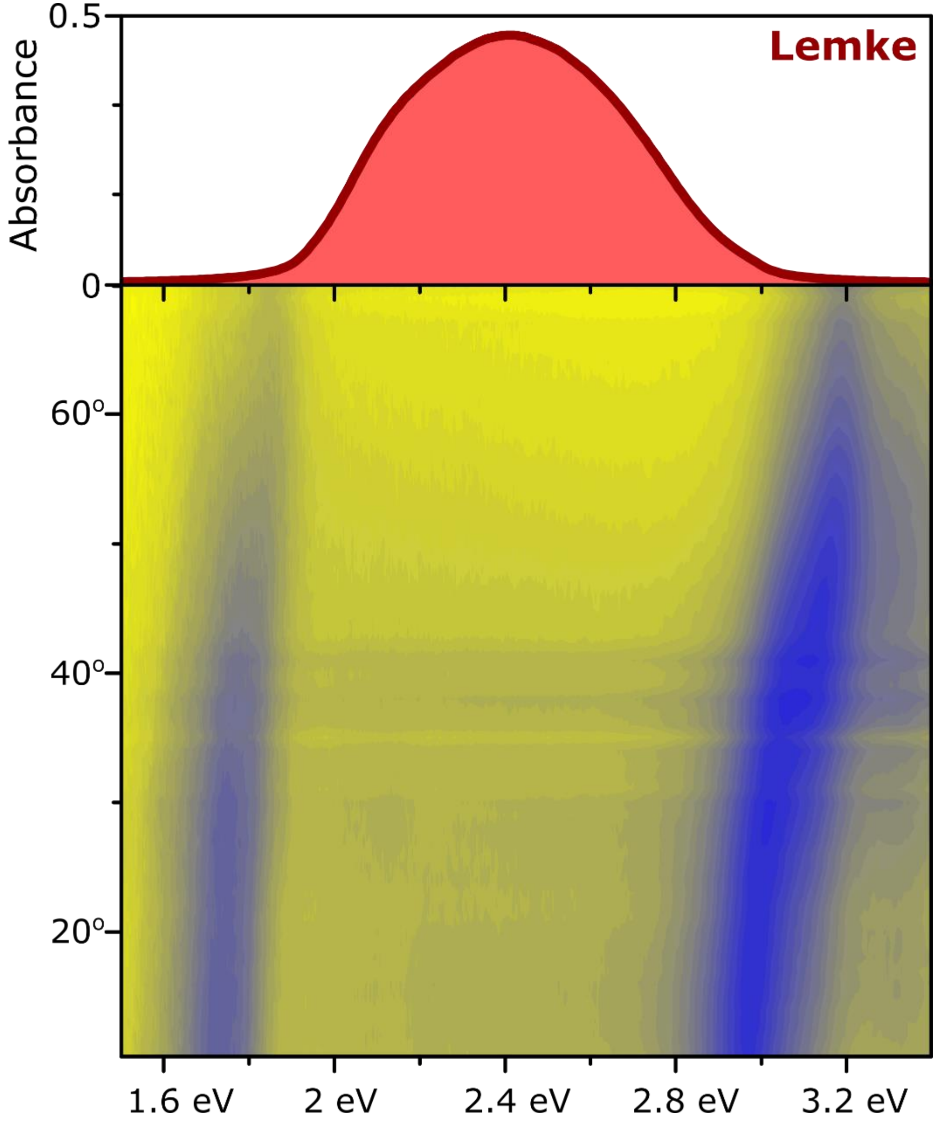


George et al., in preparation

Ultrastrong coupling with Lemke dye



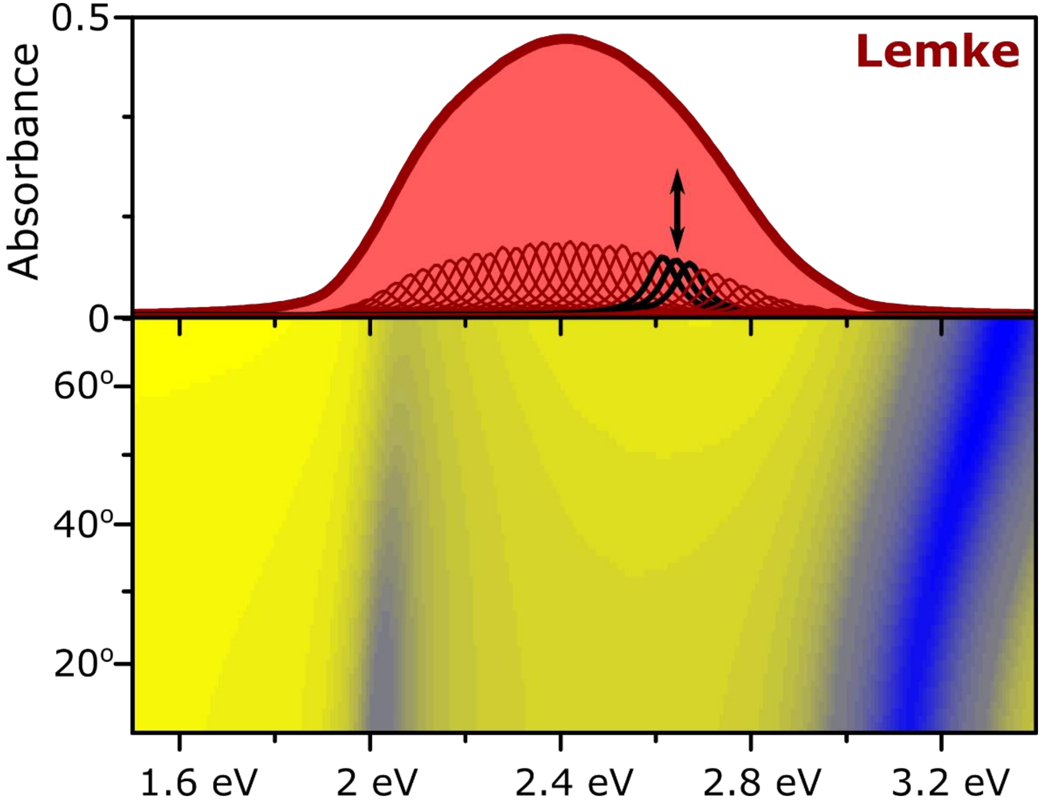
- Al-Al or Ag-Ag cavities, dye dispersed in PMMA
- Enormous splittings up to ~1.25 eV
- Describe with the same model…



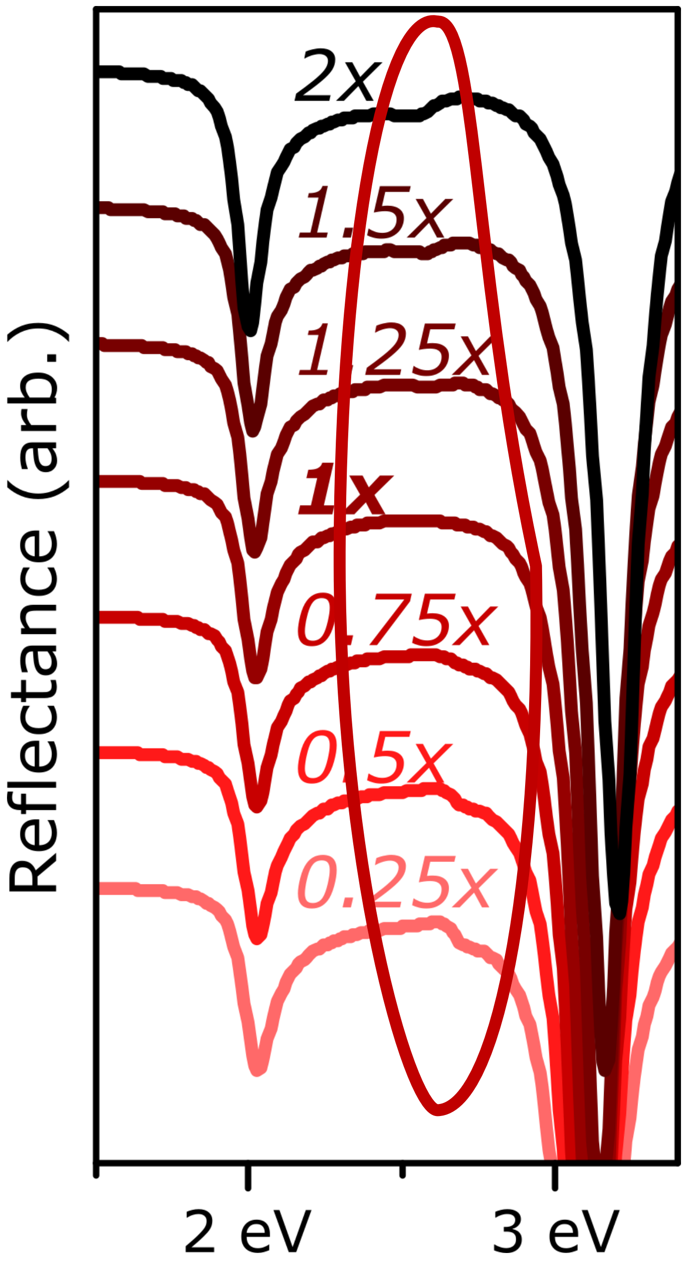
See Suzuki et al., Appl Phys Lett 2019

George et al., in preparation

‘Modifying’ Lemke dye



- New detuning, same picture
- Deviations from smooth spectrum give intermediate bands and eventual ‘MPs’



George et al., in preparation

The elephant in the cavity

- Ultrastrong coupling: g~0.2 E_{exc}
- Extend Hopfield model analogous to T-C

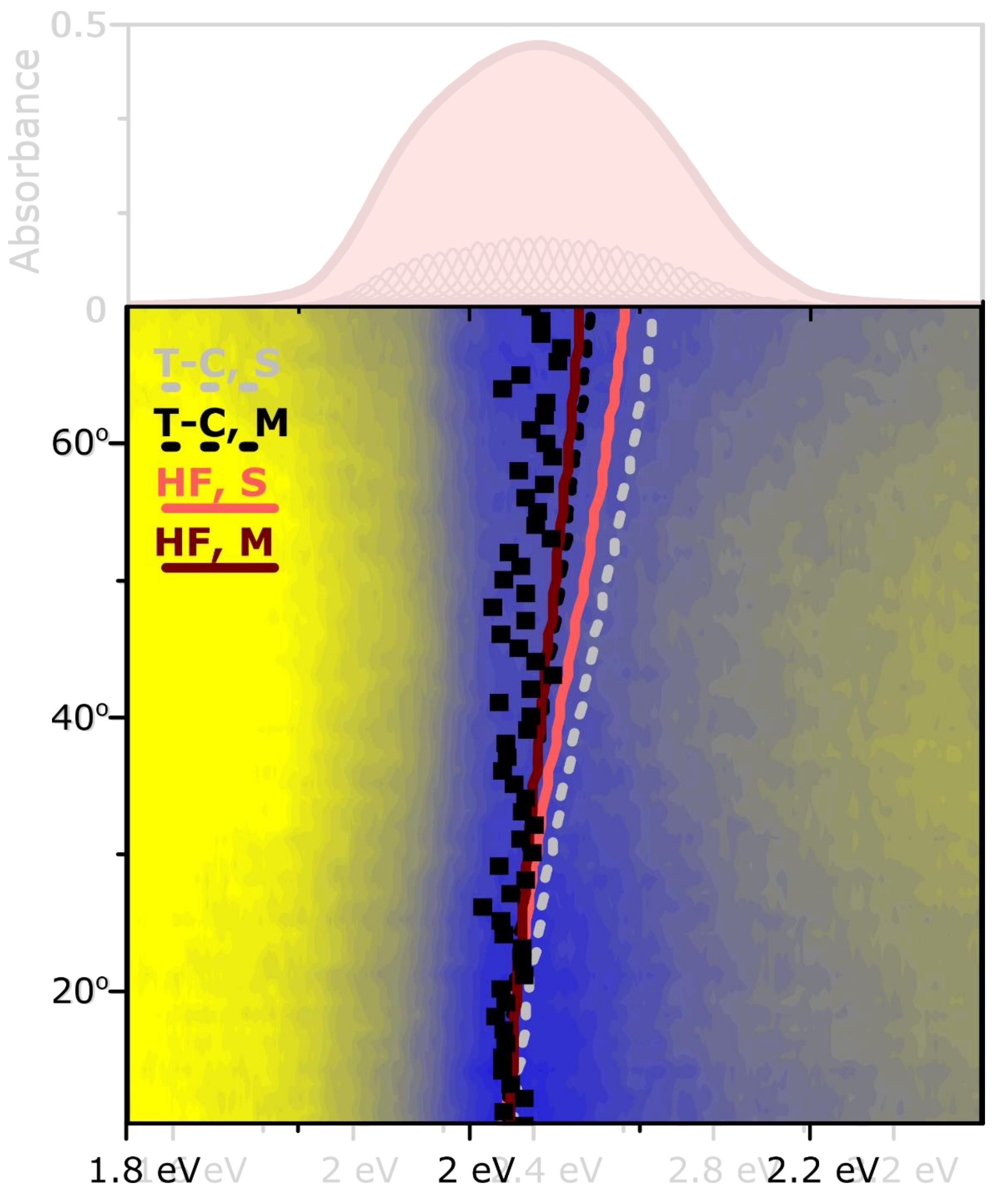
$$\begin{bmatrix} E_{ph}(\theta)+2D & -iV & -2D & -iV \\ iV & E_0 & -iV & 0 \\ 2D & -iV & -E_{ph}(\theta)-2D & -iV \\ -iV & 0 & iV & -E_0 \end{bmatrix} \begin{bmatrix} w \\ x \\ y \\ z \end{bmatrix} = E \begin{bmatrix} w \\ x \\ y \\ z \end{bmatrix}, \quad (4)$$

where,

$$V = \hbar g = \frac{\Delta E}{2}, \quad (5)$$

$$D = \hbar \frac{g^2}{\omega_0} = \frac{\Delta E^2}{4E_0}. \quad (6)$$

- Similar output for d~150-170 nm
- Flatter LP for multi-exciton models



See Suzuki et al., Appl Phys Lett 2019

George et al., in preparation