Embrace the darkness

From singlet fission to exciton-polaritons

Andrew J Musser
musser.chem.cornell.edu
ajm557@cornell.edu
Light-Matters Group @ Cornell C&CB

Grad students:
Soham Mukherjee
David Bain
Tom Khazanov
Amy Vonder Haar
Aleesha George
Rana Lomlu
Kiser Colley
Yaejin Kim

Undergraduates:
Julia Chang, MSE
Bea Pence
Vivian Ding, CBE
Gloria Davidova, AEP
Ryan Pinard
Kelly Leiby
Sean Griffin, MSE
Pedro Oliveira, Phys
Angie Huang
Shamitri Bandopadhyay

Postdocs:
Suman Gunasekaran
Juno Kim

Alumni:
Woojae Kim (Yonsei Univ.)
Scott Renken (MSc)
Trevor Geraghty (BS, OSU)

Collaborators:
Akshay Rao, Cambridge
Joel Yuen-Zhou, UCSD
Alex Chin, Sorbonne
Zhen Shen, Nanjing
Phill Milner, Cornell
Rich Robinson, Cornell
Hugo Bronstein, Cambridge
Qiuming Yu, Cornell
John Anthony, Kentucky
Satish Patil, Bangalore
Akimitsu Narita, Okinawa
Girish Lakhwani, Sydney

Aaron Li (BS, MIT)
Nicole Silver (BS, CU Boulder)
Stavrini Tsangari (BS, Arizona/Ultima Genomics)
**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*

**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
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?
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

Light-matter interaction forms hybrid states at new energies with new properties.
Unexpected effects in organic polaritons and often inexplicable

Tilting a ground-state reactivity landscape by vibrational strong coupling

A. Thomas1, L. Lethuillier-Karl1, K. Nagarajan1, R. M. A. Vergauwe1, J. George2, T. Chervy3, A. Shalabney3, E. Devaux3, C. Genet3, J. Moran5, T. W. Ebbesen1

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

Wonmi Ahn1, Johan F. Triana2, Felipe Recabal2, Felipe Herrera2,3, Blake S. Simpkins4, J. Schachenmayer4, C. Genes5, G. Pupillo5, P. Samori3 and T. W. Ebbesen1

https://doi.org/10.1038/s41567-021-22183-3

Tuning the Work-Function Via Strong Coupling

James A. Hutchison, Andrea Liscio, Tal Schwartz, Antoine Canaguier-Durand, Cyrille Genet, Vincenzo Palearo, Paolo Samori, and Thomas W. Ebbesen*
Inspired by organic electronics

Solution-processed flexible OPV

Matched energy level ✓
Solution processability ✓
Robust ✓

Chemical reaction
Interpenetration
Wetting issues

Strategies

- Bilayer interface
- Materials development
- Materials selection

△E = IPD - EA_{A} - E_{ex}
= LUMO_{D}-LUMO_{A}

Jakowetz et al., JACS 2016

Sun et al., npj Flex Elec 2022
Polariton-mediated energy transport

- **Interlayer** donor-acceptor transfer well beyond FRET radius
- **Intralayer** energy transport over 10’s μm


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

Forrest & Menon, *Adv Mater* 2020
First, some homework

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

What does an excited exciton-polariton look like?

- But \( \tau_{\text{polariton}}^{-1} \approx (1/10 \text{ fs} + 1/10 \text{ ps})^{-1} \sim 10 \text{ fs} \ldots \)
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
Familiar transient features

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

Cavity, $\lambda_{\text{exc}} = 890 \text{ nm}$

Renken, Pandya... Musser, J Chem Phys 2021
Simulating cavity excitation effects 1

- Photoexcitation produces more than just excited electronic states

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

$\Delta n_{\text{DBR}}$: change in refractive index of dielectric mirror materials

$\Delta d_{\text{cavity}}$: thermal expansion following laser pulse absorption

Bleaching: removal of ground-state population $\rightarrow$ 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

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

Popular
Trivial design
Easy to make + measure
Quick turnaround
$\tau_{\text{photon}} \sim 10 \text{ fs}$

‘Rare’
Complex, slow fabrication
Stingy spectral signatures
$\tau_{\text{photon}} \sim 100$–300 fs

Renken, Pandya... Musser, J Chem Phys 2021

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


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

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
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)
- Coherent transport time tracks with $Q$-factor

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!
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?*

![Diagram showing transport in both polariton and dark states](image)
Another kind of ‘dark’: Triplet-pair states

- Polariton formation vastly increases delayed emission in TIPS-tetracene
- Timescales correspond with $^5\text{TT}$ 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

Polak... Musser, Chem Sci 2020
Hard to pick apart

The entangled triplet pair state in acene and heteroacene materials

Chaw Keong Yong\textsuperscript{1,2}, Andrew J. Musser\textsuperscript{13}, Sam L. Bayliss\textsuperscript{1}, Steven Lukman\textsuperscript{1}, Hiroyuki Tamura\textsuperscript{4}, Olga

\begin{itemize}
  \item \textbf{Exothermic TPc:} SF is unidirectional into a dark \textsuperscript{1}TT state
  \item \textsuperscript{1}TT is very weakly bound
  \item Can be stabilised at low temperature
\end{itemize}

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

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’ $^1TT$

- T-dep at higher energies follows film
- T-dep at large detunings follows reported $^1TT$ behavior
- 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

- Exciton broadening gives broadened 'dark' states

- Disorder effects in model systems

- Eigenstates scrambled $\rightarrow$ enhanced entanglement!

- New relaxation/energy transfer pathways?

- Wellnitz et al., Comm Phys 2022


- Gera & Sebastian, J Chem Phys 2022

- Chavez et al., PRL 2021; Zeb, PRA 2022

- Son et al., Nat Commun 2022
• 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?

*DelPo et al., JPCL 2021*
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
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-coupling 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 $\sim 1.25 \text{ eV}$
- 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...

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

Musser & Clark, Annu Rev Phys Chem 2019

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

David G. Bossanyi, Maik Matthiesen, Shuangqing Wang, Joel A. Smith, Rachel C. Kilbride, James D. Shipp, Dimitri Chekulaev, Emma Holland, John E. Anthony, Jana Zaumseil, Andrew J. Musser, and Jenny Clark
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 $^1\text{TT}$ 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
- **Sub-resonant**: excite $\sim$where $^1TT$ should be

*Kim, Bain et al., under review*
Direct excitation of $^1$TT in films

Kim, Bain et al., under review
All roads lead to T+T

- Identical decay pathway once $^1TT$ is formed, regardless of how we produce it
Molecules matter

- All ‘strongly interacting’ pentacenes enable direct excitation of $^1\text{TT}$
- 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 $^1\text{TT}$ 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 $^1\text{TT}$ becomes the primary excited state?

![Diagram showing the transition from $S_0$ to $S_1$ in the conventional and coherent $^1\text{TT}$ generation pathways.](image)

**Normalized Absorbance**

- **Wavelength (nm)**
- **Norm. Abs.**

- **Graphs**
  - P DMF
  - P PS
  - PP DMF
  - PP PS
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

- Article
  Strong Coupling with Light Enhances the Photoisomerization Quantum Yield of Azobenzene

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

of additional potentialities.
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Hugo Bronstein, Cambridge  
Qiuming Yu, Cornell  
John Anthony, Kentucky  
Satish Patil, Bangalore  
Akimitsu Narita, Okinawa  
Girish Lakhwani, Sydney

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Chemical Sciences, Biosciences, and Geosciences Division
Different flavors of delocalization?

Long-Range Transport of Organic Exciton-Polaritons Revealed by Ultrafast Microscopy
Georgi Gary Rozenman, Katherine Akulov, Adina Golombek, and T.J. Schwartz

Wavefunction Overlap

Increased spatial extent

Polaritons
Dark States

(c) Spatiotemporally-integrated Width (µm)

Pump-probe delay (ps)

0 2 4 6 8 10

TM polaritons
TE polaritons
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

- Triplet photoinduced absorption, Stern Nat Chem 2017
- Delayed $S_1$ emission, Stern Nat Chem 2017
- Free triplet EPR signature, Weiss Nat Phys 2017
- $^5$TT EPR signature, Weiss Nat Phys 2017

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

Polak... Musser, Chem Sci 2020
Quintet ‘harvesting’? Rate model

- Bulk of population resides in pool of high-spin TT\textsubscript{dark}

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

$k_{SF} \approx (50\text{ps})^{-1}$, $k_{SF} \approx (1\text{ns})^{-1}$

$k_{\text{dark}} \approx (30\text{ns})^{-1} \rightarrow k_{\text{dark}}$

$k_{\text{pol}_s} \approx k_{\text{pol}_b} \approx (100\text{ns})^{-1}$

$k_{\text{pol}_d} \approx 0.005*k_{\text{pol}_s}$

$k_{\text{spin}} \approx (10\mu\text{s})^{-1}$

Polak... Musser, Chem Sci 2020
Emissive spin-0 triplet-pairs are a direct product of triplet-triplet annihilation in pentacene single crystals and anthradithiophene films

- Mixing with S₁, 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

\[
\Delta \sigma = \sqrt{\sigma(t_N)^2 - \sigma(t_0)^2}
\]

\[
\Delta T/T \quad \text{(norm.)}
\]

\[
\text{Position (nm)}
\]
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
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
‘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: $g \sim 0.2 \ E_{\text{exc}}$
- Extend Hopfield model analogous to T-C

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

where,

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

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

- Similar output for $d \sim 150-170 \ nm$
- Flatter LP for multi-exciton models

See Suzuki et al., Appl Phys Lett 2019

George et al., in preparation