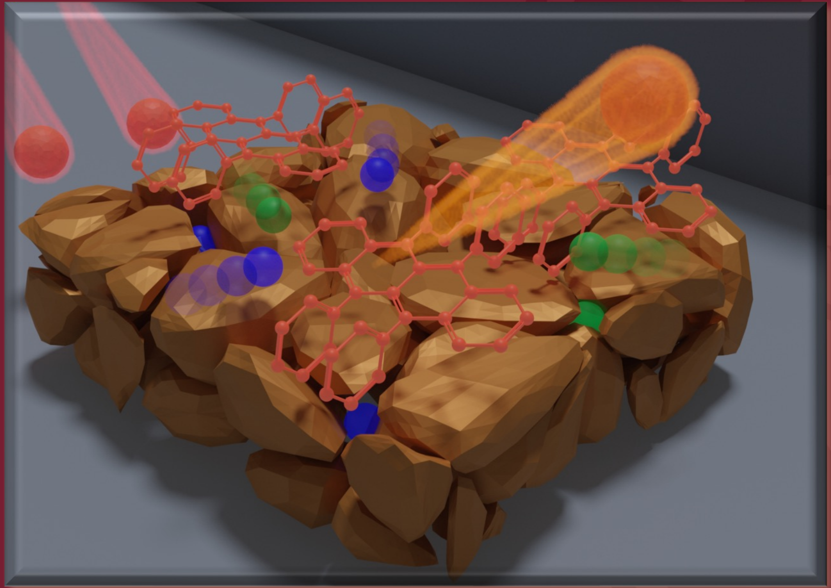
FLORIDA STATE UNIVERSITY

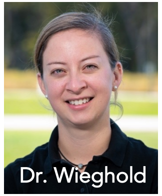
Research in the Nienhaus Lab



Lea Nienhaus
Florida State University
Department of Chemistry and Biochemistry

Florida State University
June 27th, 2023

Introducing the Nienhaus Lab (Est. 2018)



- Light-Matter Interactions: Macroscale vs. Nanoscale
  - Nanocrystals
    - Triplet Sensitization
      - CdSe Nanoplatelets
        - Lateral Size
        - Stacking
        - Shell Growth
      - CdTe Nanorods
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  - Perovskite Single Crystals
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        - New Annihilators
          - 1-Chloro BPEA
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    - Effect of Heat, Light and Electric Fields
      - STM
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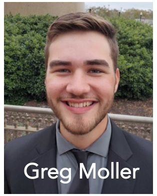
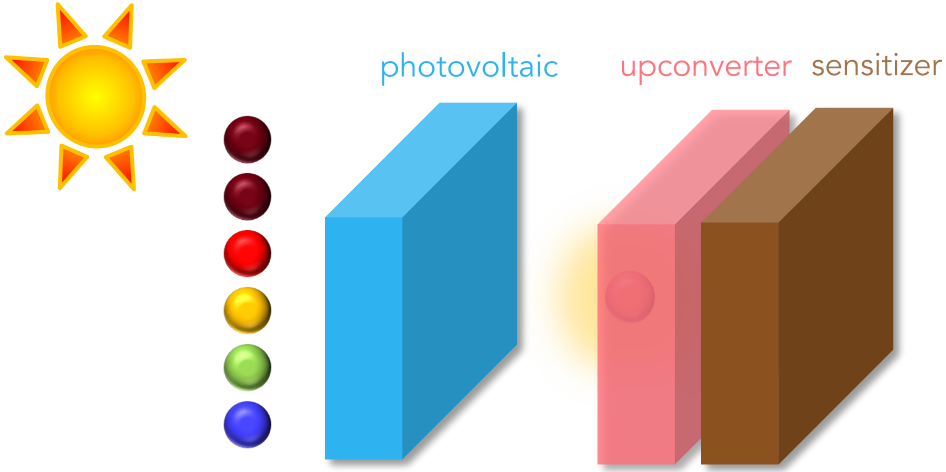
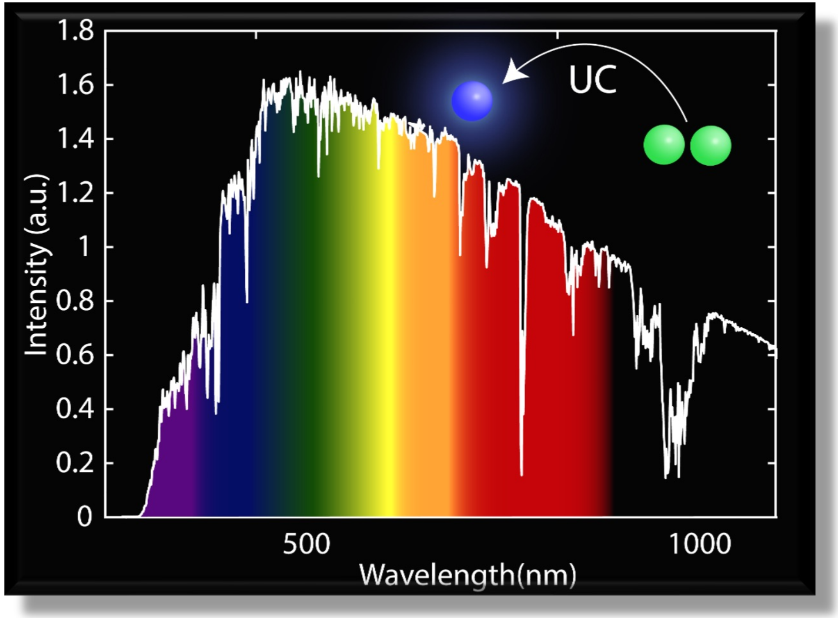


Photon Upconversion

Upconversion: combining two or more low energy photons to one higher energy photon.

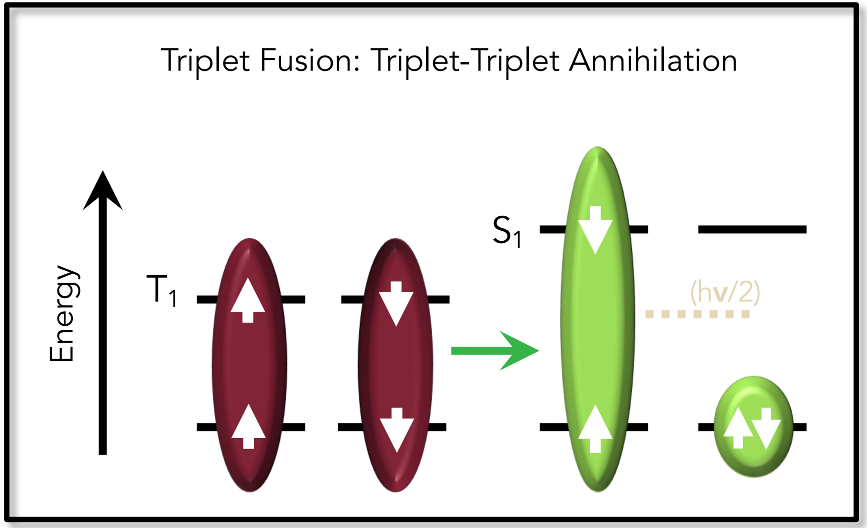


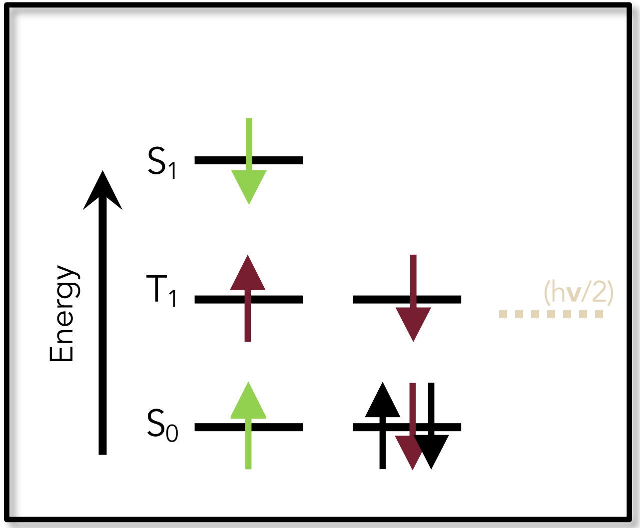


In our system upconversion occurs through triplet-triplet annihilation in organic semiconductors.

Triplet-Triplet Annihilation

Taking advantage of non-emissive, long-lived triplet states in polyacenes.
Two anti-correlated triplets interact without forbidden spin flip.





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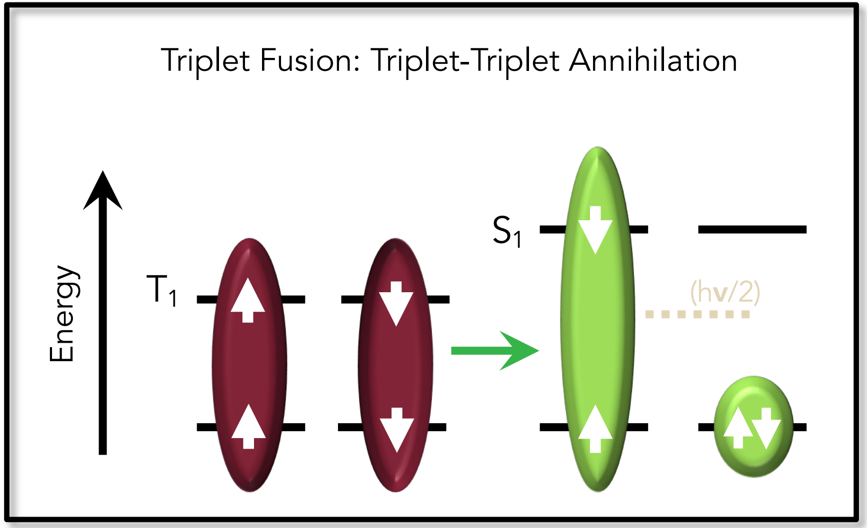
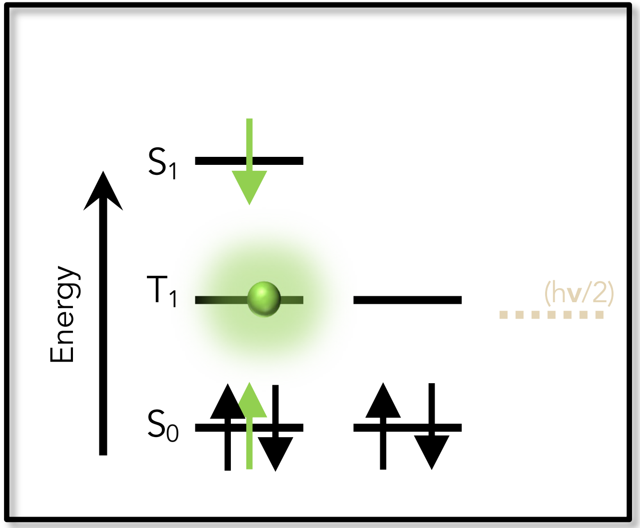


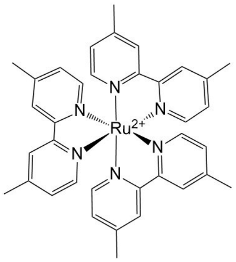


How do we efficiently access the triplet state?

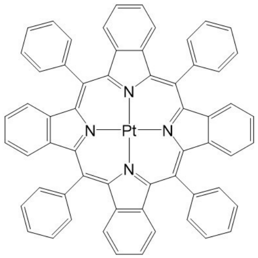
Triplet Sensitizers

Metal-organic complexes

Heavy metal facilitates ISC



Ru(dmb)$_3$

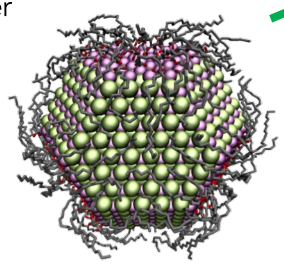


PtTPBP

Quantum Dots

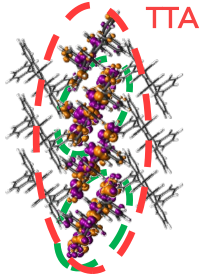
Exciton has both singlet <u>and</u> triplet character

QD (sensitizer)



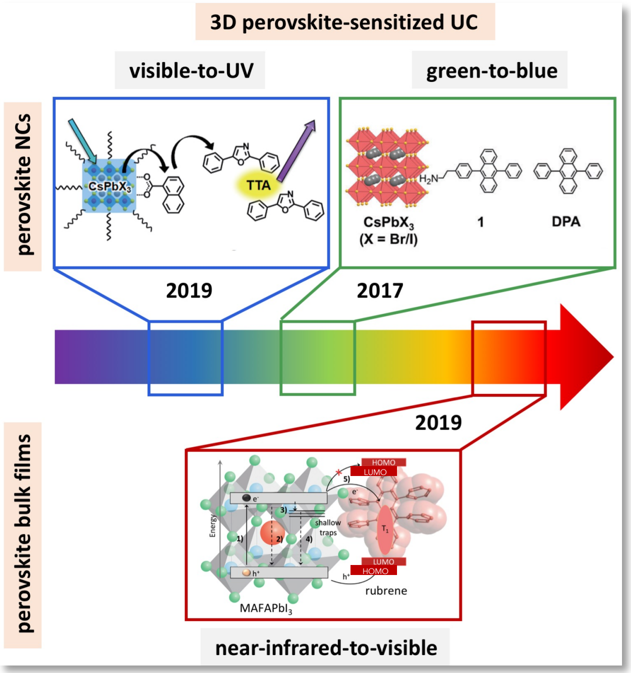
Energy transfer to triplet state

Annihilator



M. Wu *et al. Nature Photonics* **2016**

Perovskites



Wieghold, S., Nienhaus, L. *PLOS One* **2020**

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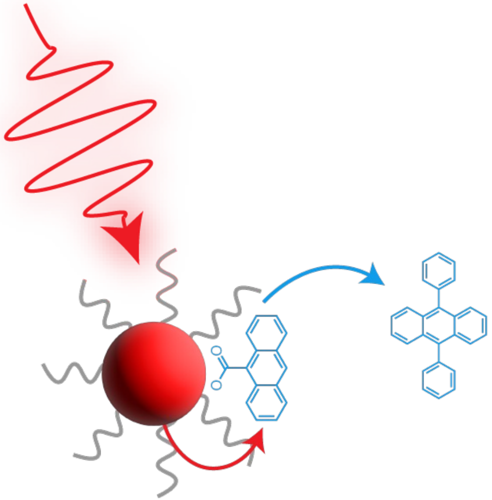
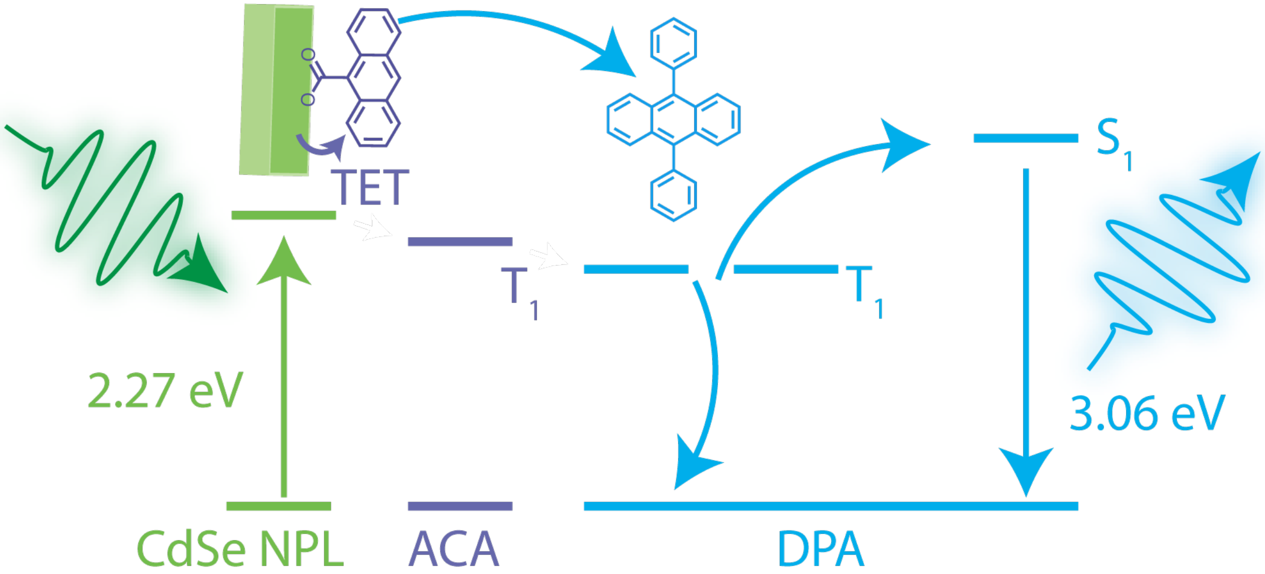
Challenges: Quantum-Confined Triplet Sensitizers

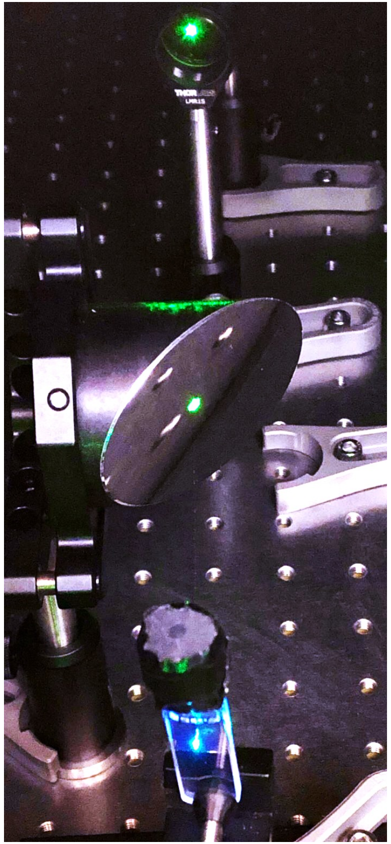


Maximize
apparent anti-
Stokes shift

Nanoplatelet Sensitizers

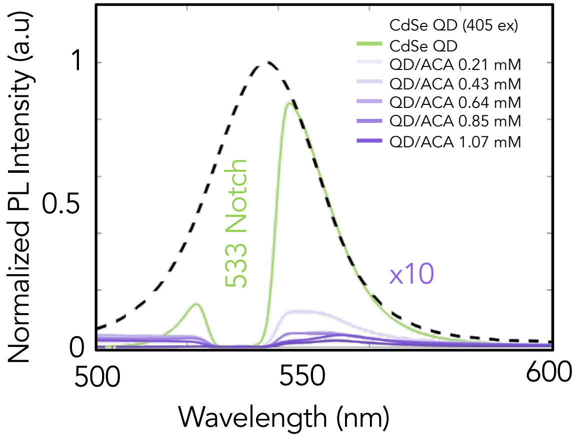


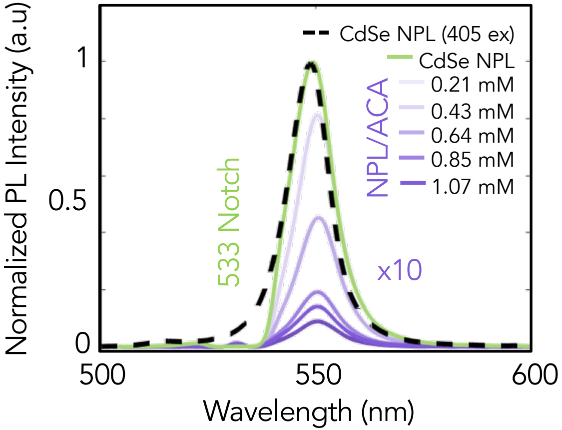
VanOrman, Z. A.; Bieber, A. S.; Wieghold, S.; Nienhaus, L. *Chem. Mater.* **2020**, *32*, 4734–4742.



Nanoplatelet Sensitizers

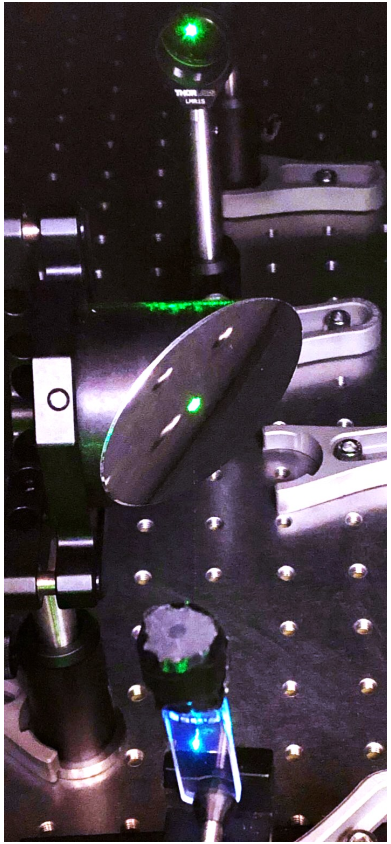
Increasing the dimensionality: 0D → 2D



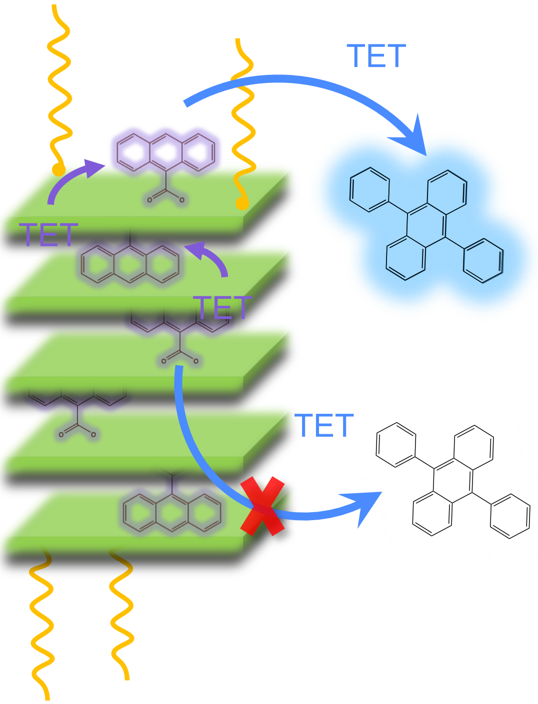


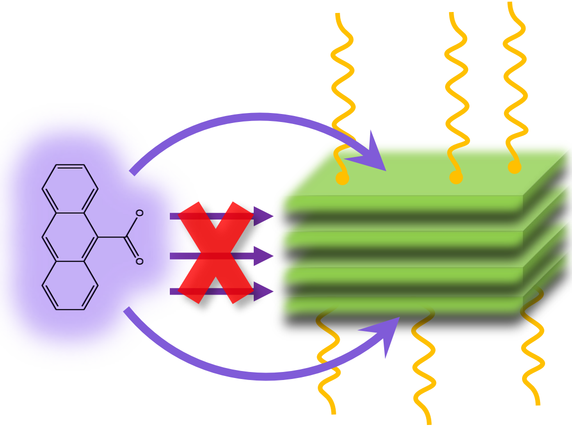
Despite the promising lower I_{th}, we see a lower UC QY for NPL sensitized UC.

VanOrman, Z. A.; Bieber, A. S.; Wieghold, S.; Nienhaus, L. *Chem. Mater.* **2020**, *32*, 4734–4742.



Nanoplatelet Sensitizers



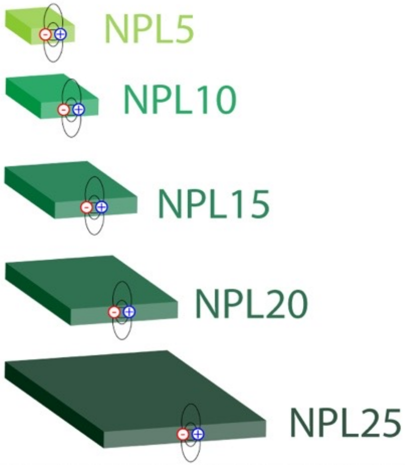


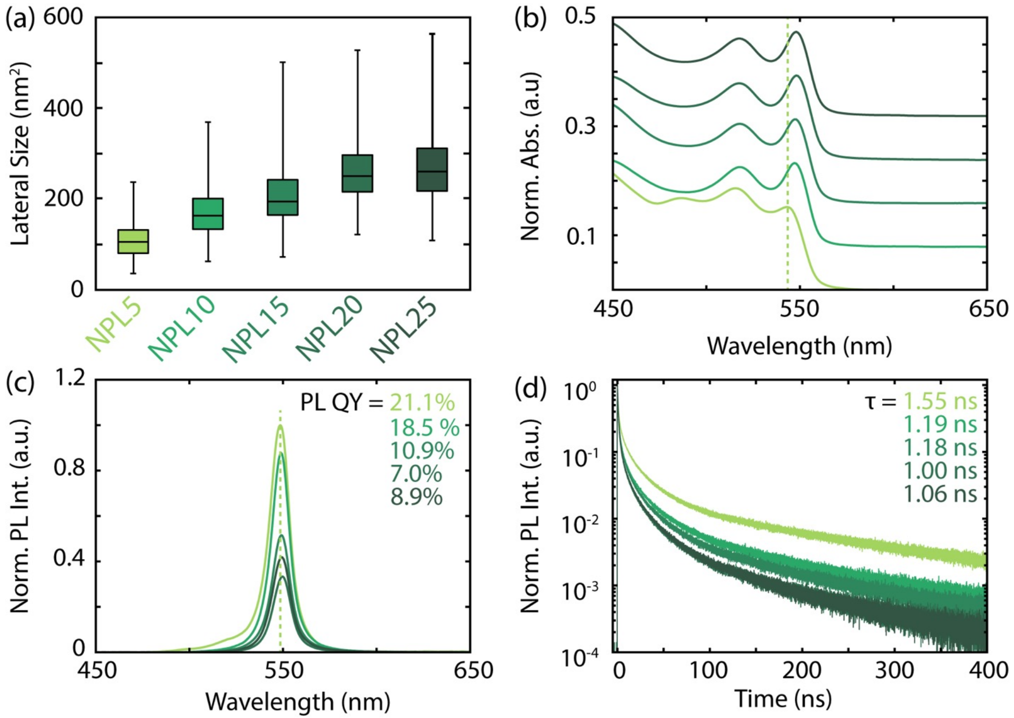
- Stacking can cause inaccessible transmitter ligands → not TET active.
- Stacking can reduce the sites transmitter ligands can bind to.

VanOrman, Z. A.; Bieber, A. S.; Wieghold, S.; Nienhaus, L. *Chem. Mater.* **2020**, *32*, 4734–4742.

Lateral Dimensions – Size Matters!

NPLs are only confined in one dimension
→ change size/absorptivity without changing energetics





VanOrman, Z. A.; Weiss, R.; Bieber, A. S.; Chen, B.; Nienhaus, L. *under review*

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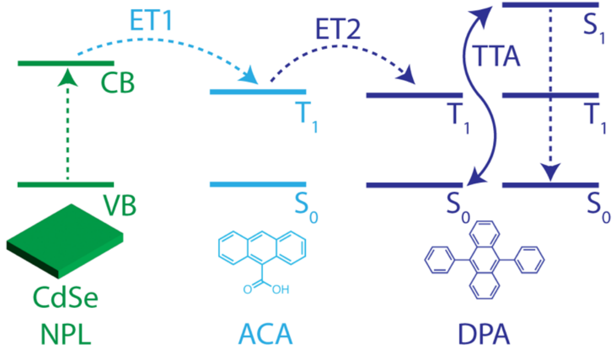
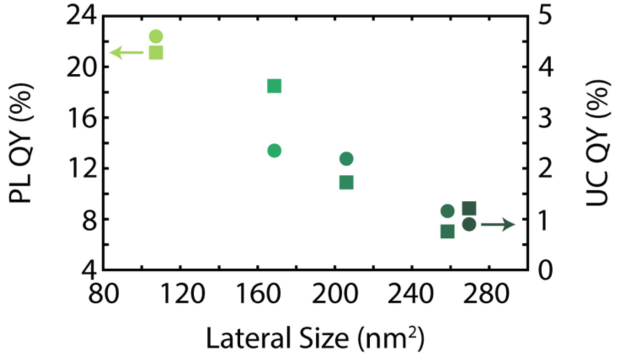
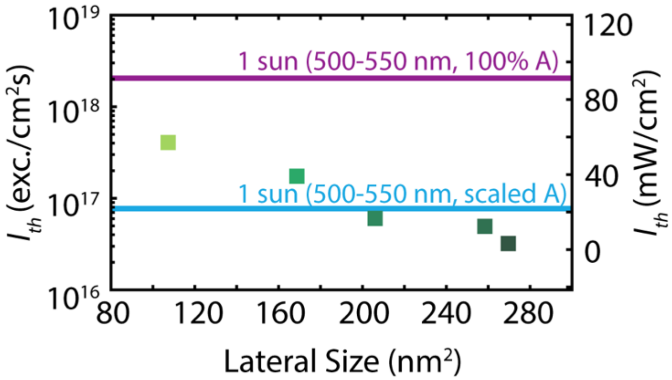




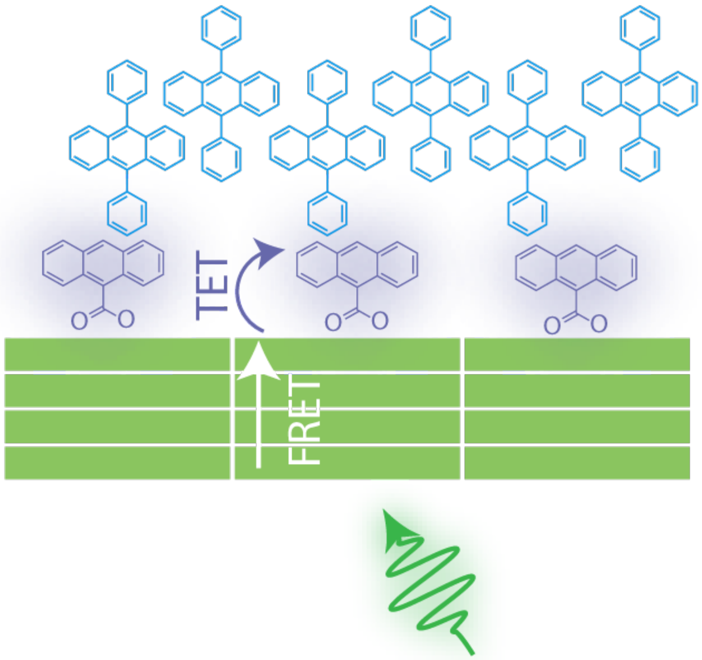


Reduction in the UC QY with increasing size is not simply due to lower PLQY:

2-fold reduction in the PLQY but 5-fold reduction in the UC QY

VanOrman, Z. A.; Weiss, R.; Bieber, A. S.; Chen, B.; Nienhaus, L. *under review*

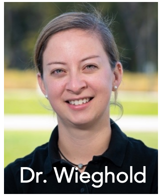
Outlook



NPLs are promising sensitizers in solid state due to the promise of rapid and efficient long-range energy transfer.

Requirement for solid-state UC device fabrication: efficient solid-state annihilators

Introducing the Nienhaus Lab (Est. 2018)



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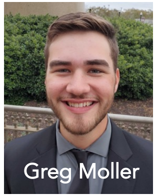
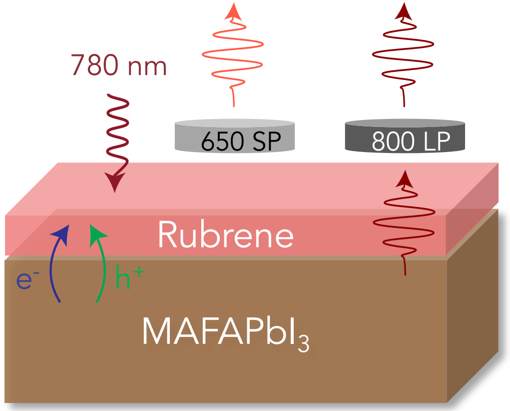
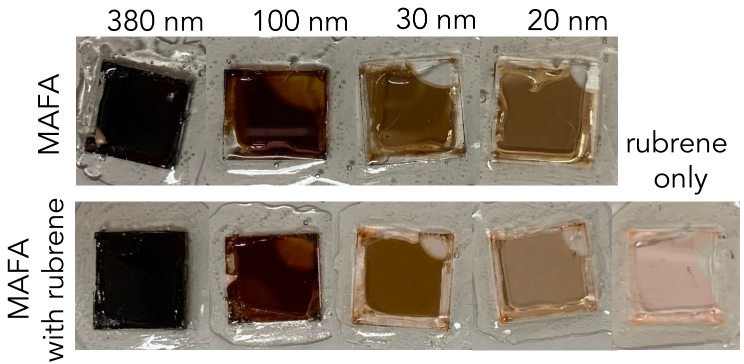
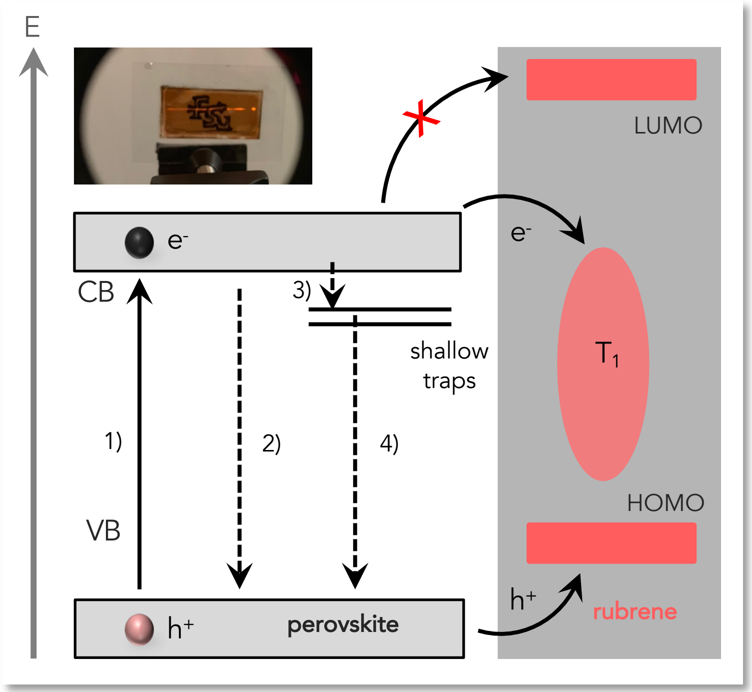


Perovskite-Sensitized Triplet Generation







Wieghold, S.; Bieber, A.S.; VanOrman, Z.A.; Daley, L.; Leger, M.; Correa-Baena, J.P.; Nienhaus, L., *Matter*, **2019**

Near-Infrared-to-Visible Upconversion

Converting infrared (low energy) light to visible (high energy) light *via* sensitized triplet-triplet annihilation.

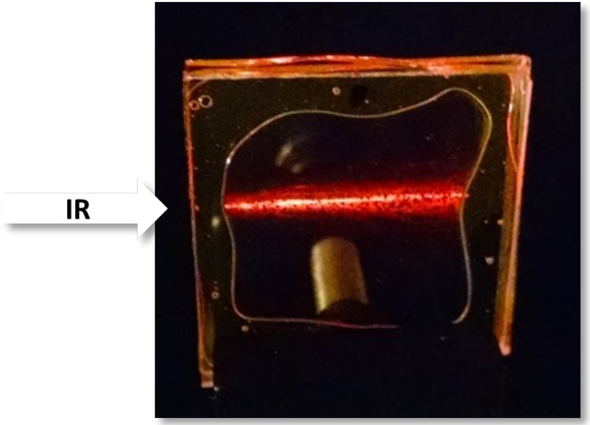
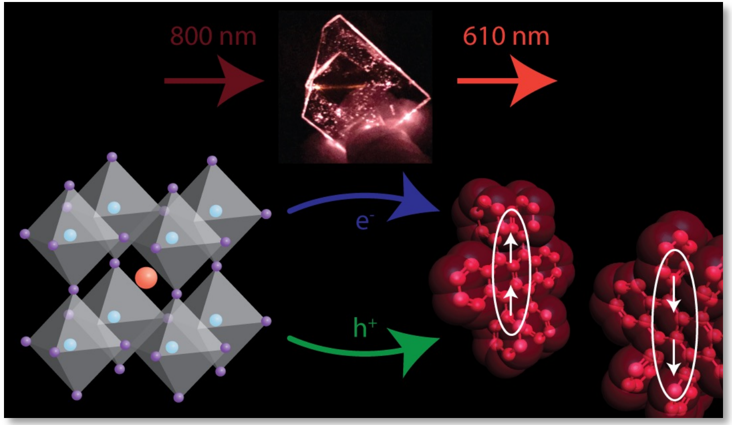


Photo: Dan Congreve

QD-based upconversion
Limited by poor exciton diffusion
Current benchmark: <1% absorption



Nienhaus, L., *et al. ACS Energy Lett.* **2019**

Perovskite-based upconversion
Current benchmark: up to 60% absorption

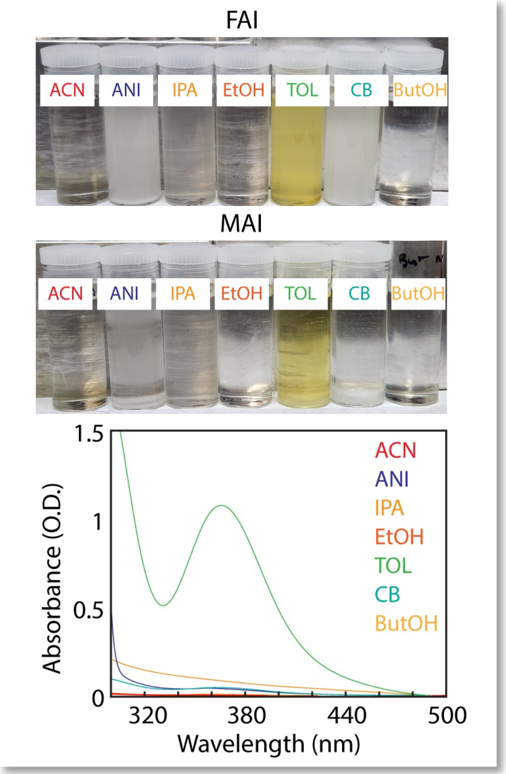
Tailoring the Perovskite/Rubrene Interface

Perovskites are very susceptible to their environment. Solvent treatment can remove individual ions, resulting in a chance in the local surface composition, which will change the electronic structure.

Solvents classified according to Taylor et al.: (*Nat. Commun.* 12, 1878 (2021))

Type I: dissolve MAI/FAI → PbI_2 generation
Type II: do not dissolve MAI/FAI or PbI_2
Type III: generate I_3^-

ACN: dissolves both MAI/FAI and PbI_2 once sufficient MAI/FAI is dissolved.



Sullivan, C.M., Bieber, A.S., Drozdick, H.K., Moller, G., Kuszynski, J.E., VanOrman, Z.A., Wieghold, S., Strouse, G.F. Nienhaus, L. *Adv. Opt. Mater.* **2023**

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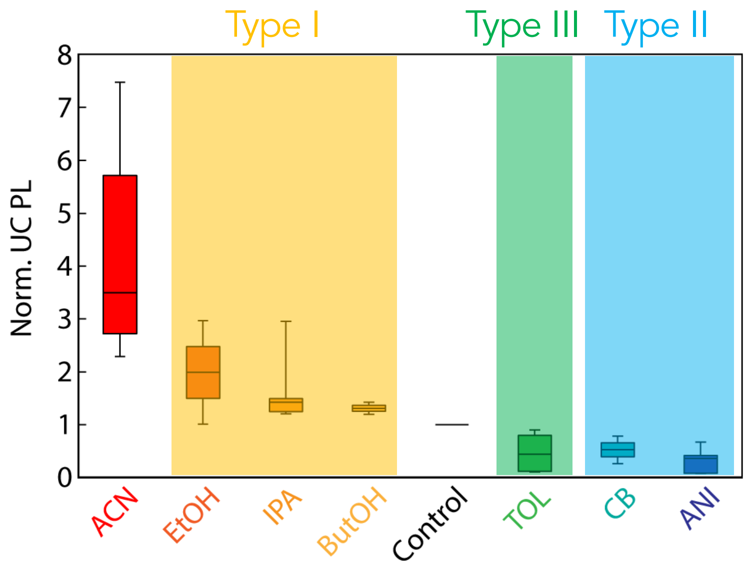

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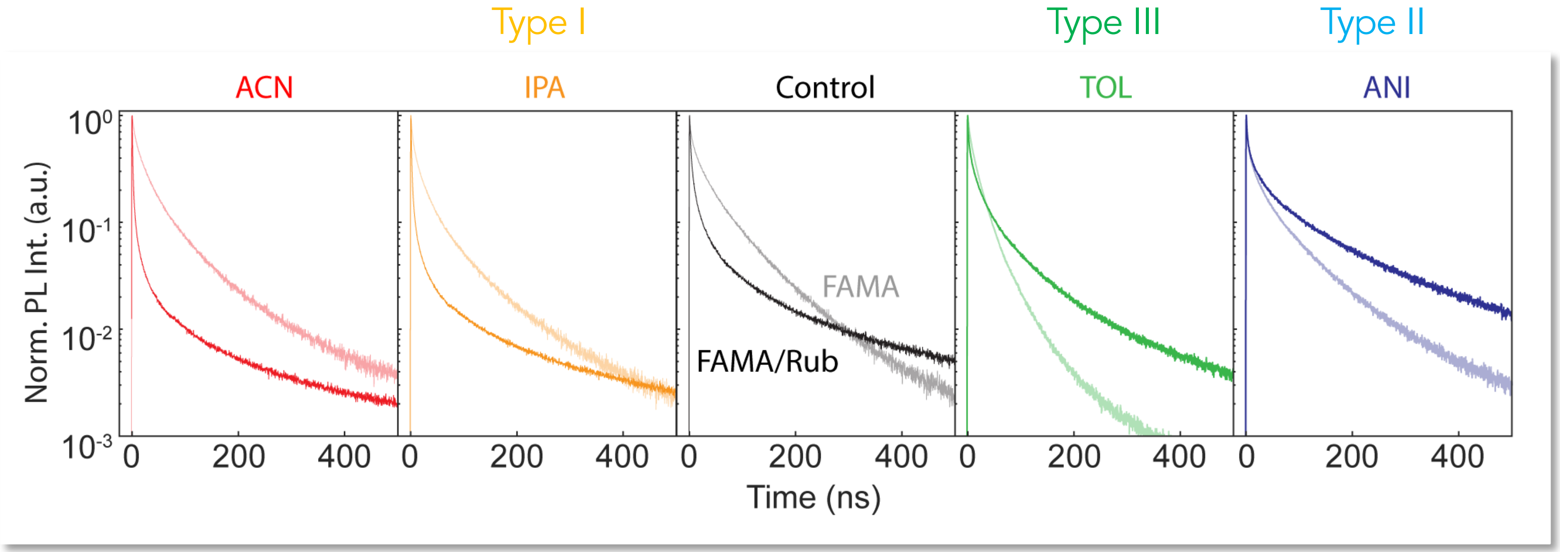
Tailoring the Perovskite/Rubrene Interface

In agreement with the increased UC PL intensity, we find higher amounts of quenching for Type I solvents, while Type II and Type III solvents reduce the amount of quenching.



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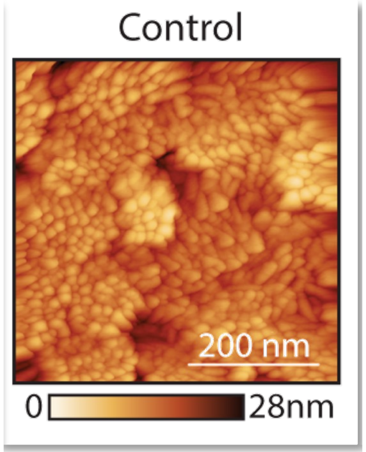
Tailoring the Perovskite/Rubrene Interface

XRD shows removal of the undesired **δ**-phase with Type I solvents and ACN.

Does the removal of individual ions result in a change in the surface morphology? Is a 2D perovskite structure grown over the 3D perovskite? Is there a rearrangement at the surface?



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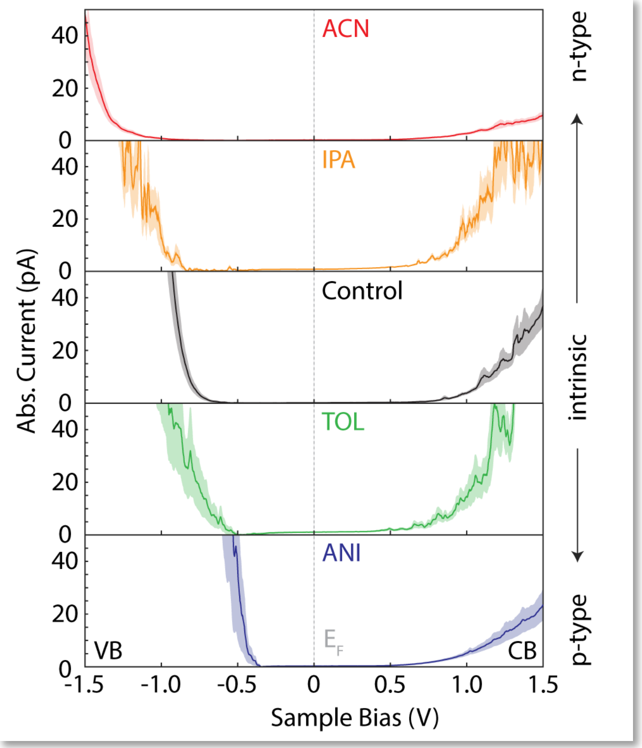
Tailoring the Perovskite/Rubrene Interface

The presence of defects and PbI_2 influence the electronic structure of the perovskite surface.

Defects and PbI_2 can induce doping, hence affect the interfacial band bending.

The change in E_F will greatly influence the band alignment at the perovskite/rubrene interface and thus, the charge transfer.

We propose that interfacial defects do not inherently mediate the charge transfer but result in improved charge extraction due to the interfacial energy alignment.



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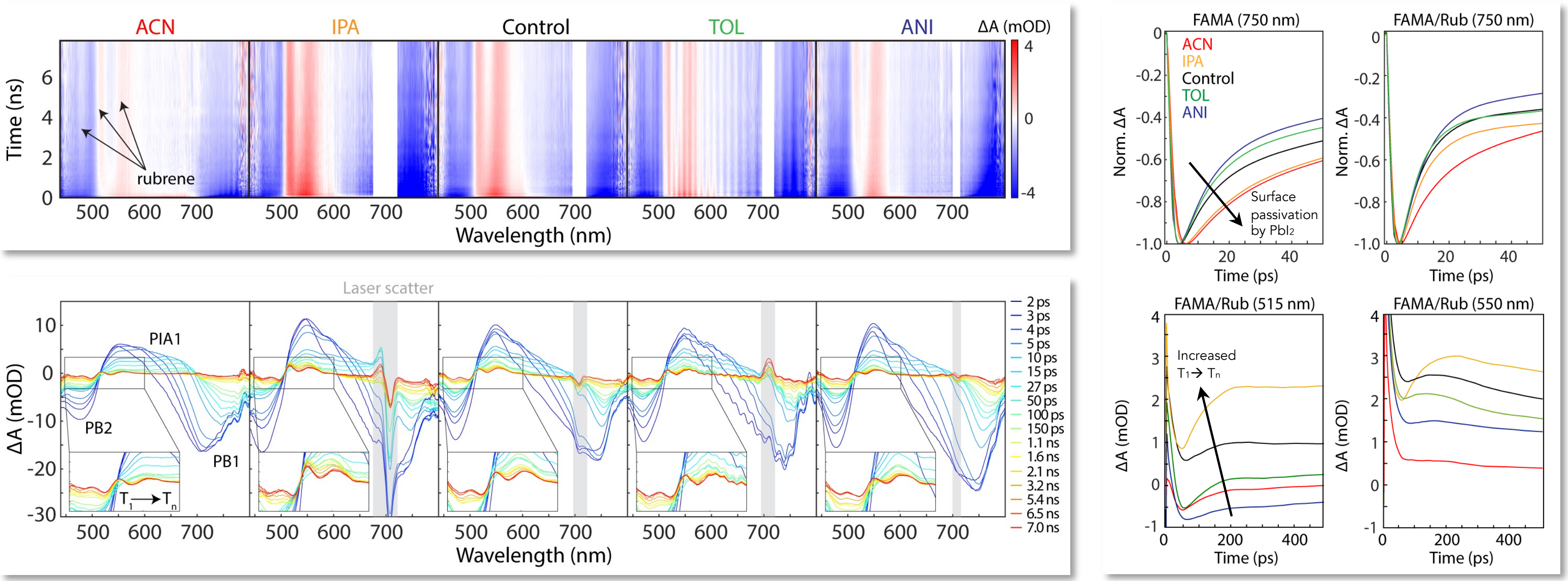

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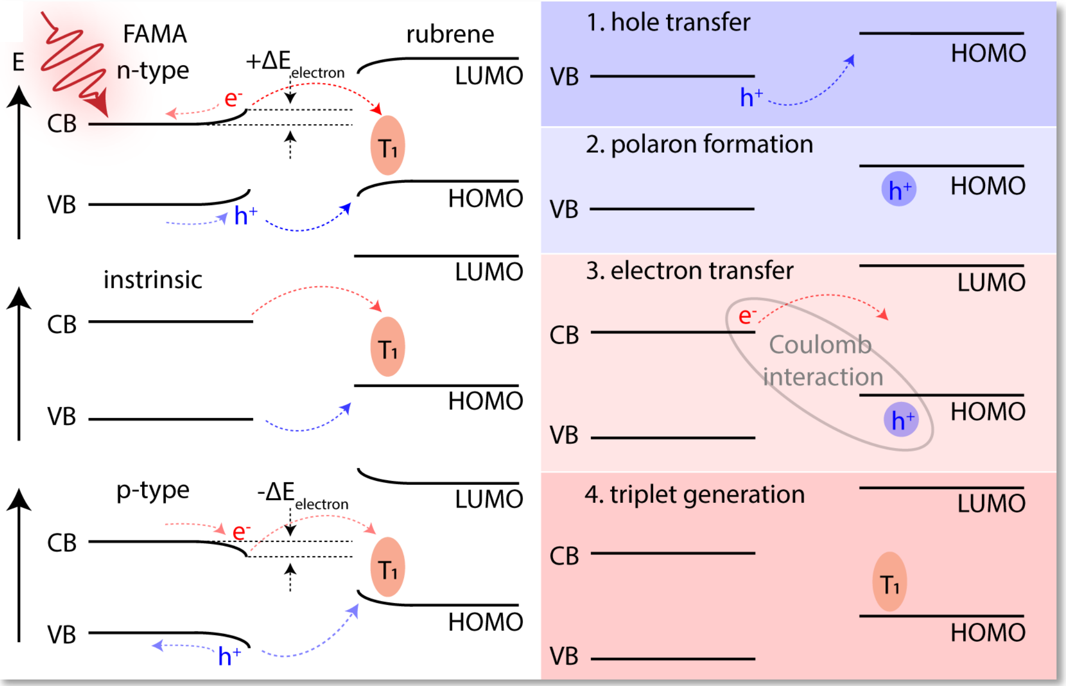
Tailoring the Perovskite/Rubrene Interface

The presence of defects and PbI_2 influence the electronic structure of the perovskite surface.

n-type doping results in hole accumulation at the surface.

p-type doping results in holes accumulating in the bulk.

→ Changes in the interfacial charge extraction



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Next-Generation Annihilators

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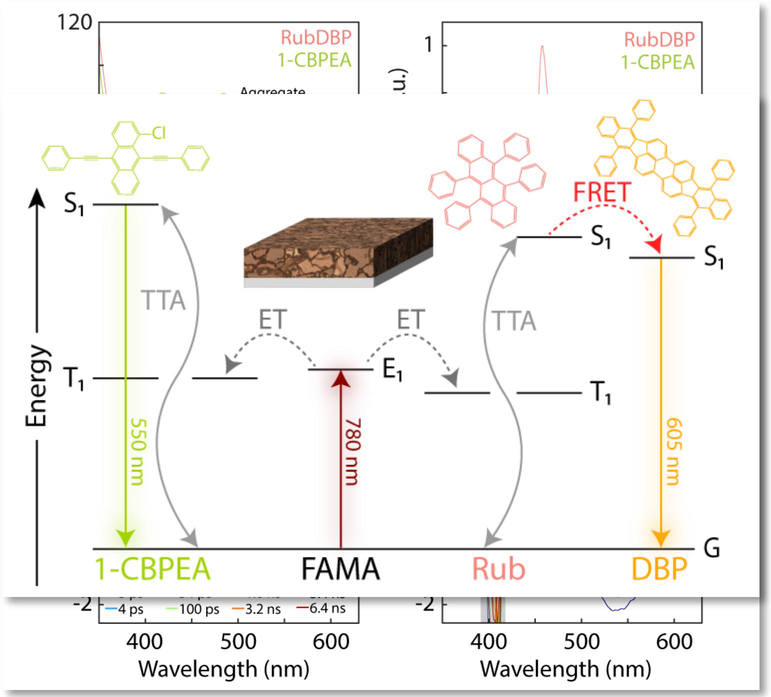
Next-Generation Annihilators



Sullivan, C.M.; Nienhaus, L. *Nanoscale*, **2023**

Due to the limited achievable apparent anti-Stokes shift (800 nm → 565 nm/605 nm) the rubrene/DBP pair is not well matched to the iodide-based perovskite.

Ideally, an annihilator with $T_1 \approx 1.5$ eV is desired.

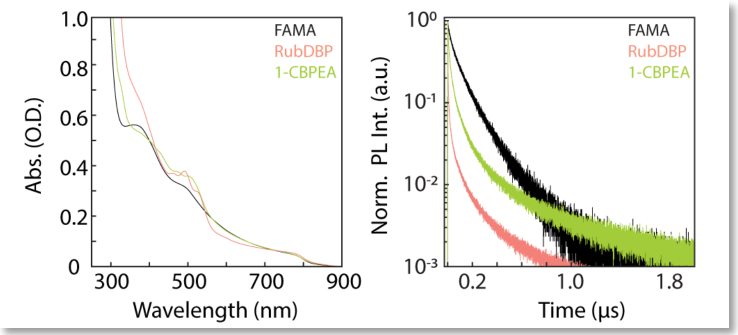
However, many successful solution-based annihilators do not show the same results in solid state (e.g., DPA is plagued by excimer formation).

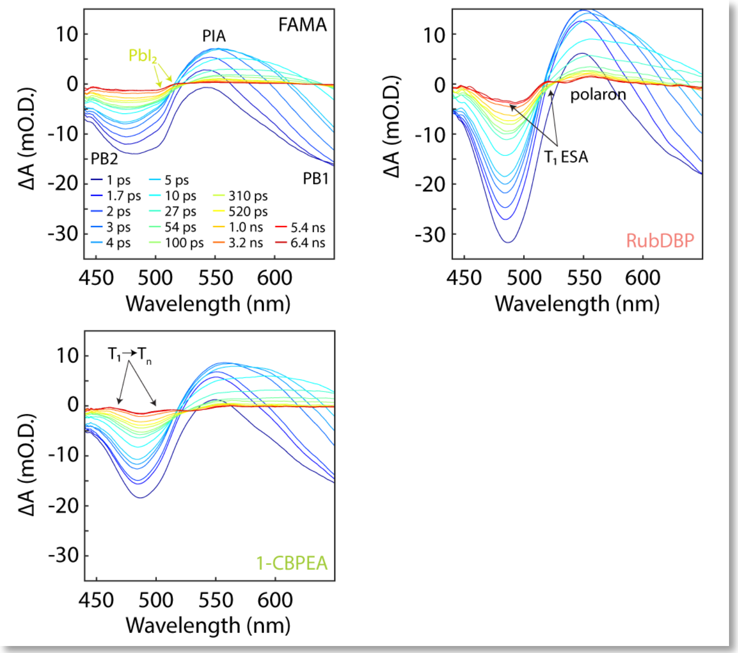
1-chloro-9,10-bis(phenylethynyl)anthracene (T_1 = 1.2 eV is a promising step towards expanding the compatible solid-state annihilator library.

Next-Generation Annihilators

PL quenching is promising, but not sufficient to determine whether the triplet is created.

PL quenching could also indicate single charge (hole) extraction.





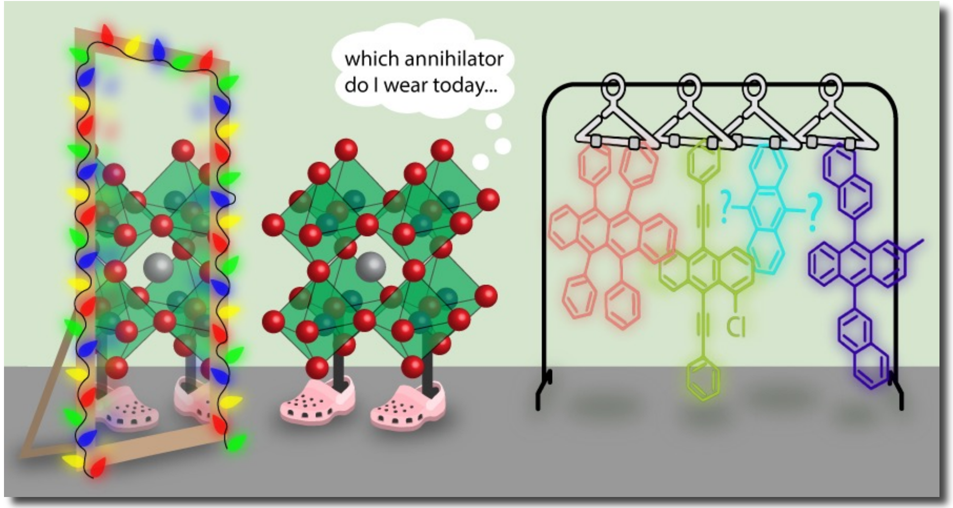
Summary and Outlook

Progress is being made in understanding triplet generation at the perovskite/organic interface.

The mechanism of triplet generation based on free carrier injection has been understood.

New annihilators have been identified. More to come, stay tuned…

Open questions: role of nanoscale OSC arrangement and coupling. Aggregation-induced effects? Strong coupling vs. weak coupling?



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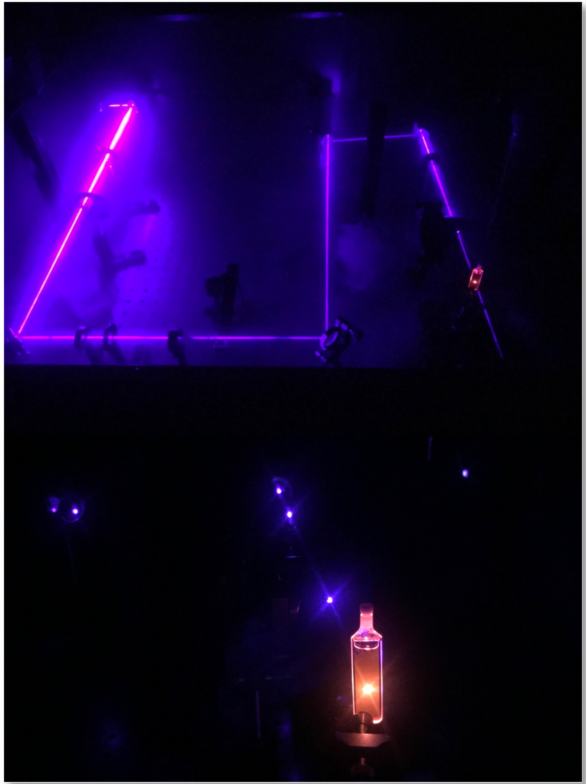
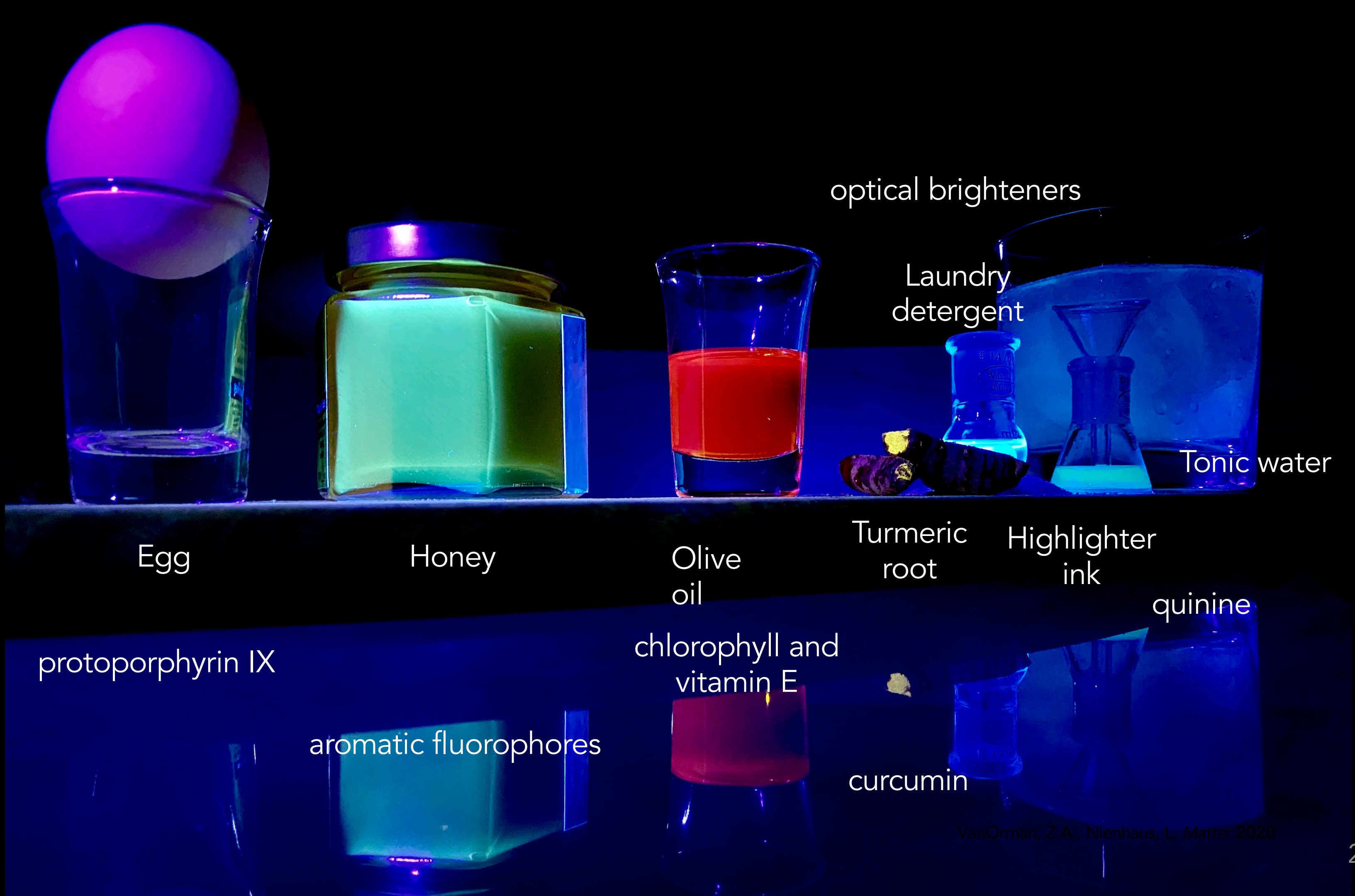
Kitchen Spectroscopy



from
lab to
kitchen

Glow from home: C&EN Chem Pics May 2020


optical brighteners
Laundry
detergent
Tonic water
Egg
Honey
Olive
oil
Turmeric
root
Highlighter
ink
quinine
protoporphyrin IX
chlorophyll and
vitamin E
aromatic fluorophores
curcumin
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Prof. Dr. Uli Nienhaus
Dr. Karin Nienhaus
Dr. Jens Lackner

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