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
  - FAMA
  - Mixed Halide

- Nanoplatelets
  - SMA-STM
  - Shell Growth
  - Composition
  - MAFA

- CdTe Nanorods
  - Triplet Sensitization
  - Crystal Structure
  - CsFA
  - Thermal Annealing
  - Rubrene Deposition

- Device Fabrication
  - Composition
  - Fabrication Methods
  - One Step
  - Role of DBP
  - Rubrene Solvent Treatment

- Bulk Perovskites
  - Triplet Sensitization
  - Transition Metal Doping
  - Bulk Perovskite
  - Mechanistic Insights
  - Rubrene
  - New Annihilators
  - 1-Chloro BPEA
  - STM

- Perovskite Single Crystals
  - SMA-STM
  - SX-STM
  - SMA-STM
  - Soft X-Ray

- Bulk Perovskites
  - Operando Conditions
  - Role of DBP
  - Heating
  - Cooling

- STM
  - SMA-STM
  - SX-STM

- Transition Metal Doping
  - Effect of Heat, Light and Electric Fields

- SMA-STM
  - SX-STM
  - Rubrene
  - Rubrene Deposition Solvent

- GAMA
  - Mixed Halide
  - CsFA
  - Thermal Annealing
  - Rubrene Solvent Treatment

- Computation
  - Role of DBP
  - Operando Conditions
  - Heating
  - Cooling

- Dr. Wieghold
  - Alex Bieber
  - Zach VanOrman
  - Rachel Weiss Clark
  - Colette Sullivan
  - Greg Moller

- FLORIDA STATE UNIVERSITY
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.
Triplet-Triplet Annihilation

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

How do we efficiently access the triplet state?
Triplet Sensitizers

Metal-organic complexes

Heavy metal facilitates ISC

Quantum Dots

Exciton has both singlet and triplet character

Perovskites

Energy transfer to triplet state


Wieghold, S., Nienhaus, L. PLOS One 2020
Introducing the Nienhaus Lab (Est. 2018)

Light-Matter Interactions: Macroscale vs. Nanoscale

Nanocrystals
- Triplet Sensitization
  - CdSe Nanoplatelets
  - Lateral Size
  - Stacking

SMA-STM
- CdTe Nanorods
- Shell Growth
- Composition

Perovskite Single Crystals
- Triplet Sensitization
  - Device Fabrication
- Crystal Structure
- Fabrication Methods
  - Thermal Annealing
  - Rubrene Deposition

Bulk Perovskites
- Triplet Sensitization
  - Transition Metal Doping
- Transition Metal Doping
  - Role of DBP
- Solvent
  - One Step
- Role of DBP
- Operando Conditions

Effect of Heat, Light and Electric Fields
- Mechanistic Insights
  - Rubrene
  - New Annihilators
  - 1-Chloro BPEA
  - DBP

STM
- SMA-STM
- SX-STM
- Heating
- Cooling
Challenges: Quantum-Confined Triplet Sensitizers

Maximize apparent anti-Stokes shift
Nanoplatelet Sensitizers

Increasing the dimensionality: 0D → 2D

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

Nanoplatelet Sensitizers

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

Lateral Dimensions – Size Matters!

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

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

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)

Light-Matter Interactions: Macroscale vs. Nanoscale

- Nanocrystals
  - Triplet Sensitization
    - CdSe Nanoplatelets
      - Lateral Size
      - Stacking
    - CdTe Nanorods
      - Shell Growth
      - Composition
  - SMA-STM
    - Device Fabrication
      - Fabrication Methods
      - Rubrene Deposition
        - Solvent
        - Solvent Treatment
  - FAMA
    - Mixed Halide
      - MAFA
      - CsFA
        - Thermal Annealing
        - One Step
        - Role of DBP
      - Rubrene
        - Solvent
        - Heping
        - Cooling
  - Bulk Perovskites
    - Crystal Structure
    - Transition Metal Doping
      - Mechanistic Insights
      - New Annihilators
      - Rubrene
      - SMA-STM
      - SX-STM
    - STM
  - Bulk Perovskites
    - Device Fabrication
      - Operando Conditions
      - 1-Chloro BPEA
      - ??
      - 14
      - Heat, Light and Electric Fields

Dr. Wieghold
- Zach VanOrman
- Colette Sullivan
- Alex Bieber
- Greg Moller
- Zach VanOrman
- Dr. Wieghold
- Alex Bieber
- Colette Sullivan
- Greg Moller
Perovskite-Sensitized Triplet Generation

Near-Infrared-to-Visible Upconversion

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

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

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

Photo: Dan Congreve

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 \( \rightarrow \) 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.
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 → PbI₂ generation
Type II: do not dissolve MAI/FAI or PbI₂
Type III: generate I₃⁻

ACN: dissolves both MAI/FAI and PbI₂ once sufficient MAI/FAI is dissolved.
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.
XRD shows removal of the undesired $\delta$-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?
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.*
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

Next-Generation Annihilators

Light-Matter Interactions: Macroscale vs. Nanoscale

Nanocrystals
- Triplet Sensitization
  - CdSe Nanoplatelets
  - Lateral Size
- Stacking
- Shell Growth
  - CdTe Nanorods
  - Composition
    - FAMA
      - Mixed Halide
    - MAFA
    - CsFA

Perovskite Single Crystals
- Triplet Sensitization
  - Crystal Structure
- Fabrication Methods
  - Rubrene Deposition Solvent
  - Solvent Treatment
  - One Step
  - Role of DBP
  - Operando Conditions
  - Heating
  - Cooling

Bulk Perovskites
- Triplet Sensitization
- Transition Metal Doping
- Mechanistic Insights
  - Rubrene
  - New Annihilators
  - 1-Chloro BPEA
  - ??

Effect of Heat, Light and Electric Fields
- SMA-STM
- SX-STM
- STM

Device Fabrication
- SMA-STM
- STM
- Rubrene Deposition Solvent
- Solvent Treatment
- One Step
- Role of DBP
- Operando Conditions
- Heating
- Cooling

Transition Metal Doping
- New Annihilators
- 1-Chloro BPEA
- ??

Operando Conditions
- Heating
- Cooling

Mixed Halide
- FAMA
- MAFA
- CsFA

Composition
- Lateral Size
- Stacking
- Shell Growth

Effect of Heat, Light and Electric Fields
- SMA-STM
- SX-STM
- STM
Next-Generation Annihilators

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.
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?

Sullivan, C.M.; Nienhaus, L. Nanoscale, 2023
Kitchen Spectroscopy

from lab to kitchen

Glow from home: C&EN Chem Pics May 2020
VanOrman, Z.A.; Nienhaus, L. Matter 2020
Acknowledgements

FSU
Dr. Sarah Wieghold
Dr. Alex Bieber
Dr. Zach VanOrman
Colette Sullivan
Rachel Weiss
Greg Moller
Jason Kuszynski
Prof. Dr. Geoff Strouse
Prof. Dr. Theo Siegrist
Dr. Xinsong Lin

Collaborators
KIT
Prof. Dr. Uli Nienhaus
Dr. Karin Nienhaus
Dr. Jens Lackner

GA Tech
Prof. Dr. Juan-Pablo Correa-Baena

Boulder
Dr. Katherine Shulenberger

Argonne
Dr. Richard Schaller
Dr. Sarah Wieghold

Funding

NSF
DMR-2237977

Dreyfus Foundation

@NienhausFSU