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Symposium: Physical Chemistry of Semiconductor Materials and Interfaces XX

Interlayer Triplet Energy Transfer in Dion-Jacobson 2D Perovskites Containing Naphthalene Diammonium Cations

YunHui (Lisa) Lin

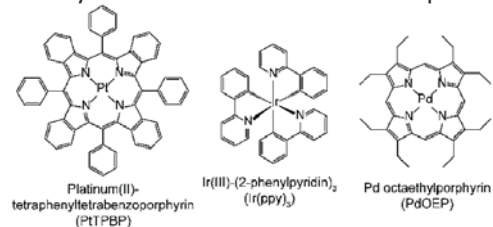
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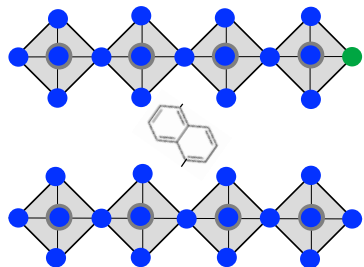
2D perovskite as a platform for triplet sensitization

- Molecular triplet excitons have many useful properties
 - Statistical abundance
 - Long lifetimes
 - Unique spin interactions
- *Triplet sensitizers* assist in populating molecular triplets

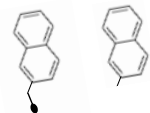
Heavy atom effect induces S-to-T spin flip



- **2D perovskites: a convenient, self-assembled framework for triplet sensitization**



Dion-Jacobson structure



Ruddlesden-Popper structure

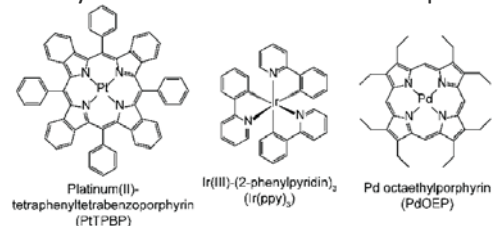
→ Inorganic Metal Halide Layer = S-T spin mixer

→ Organic Layer = triplet exciton acceptor

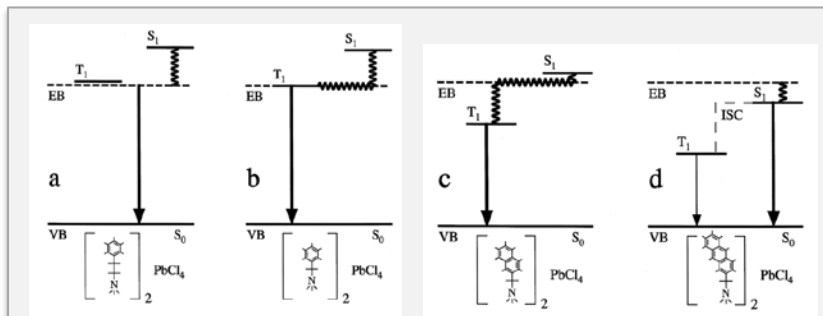
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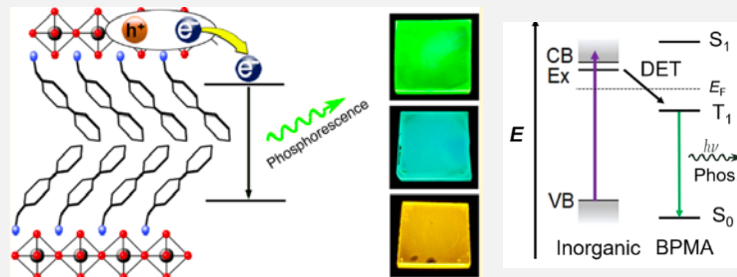
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- **2D perovskites: a convenient, self-assembled framework for triplet sensitization**



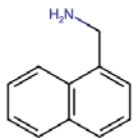
M. Braun *et al*, Chem. Phys. Lett. 303, 157 (1999)



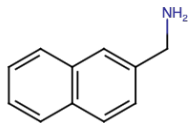
H. Hu *et al*, Chem. Mater. 31, 2597 (2019)

Naphthalene-based Ruddlesden-Popper perovskite

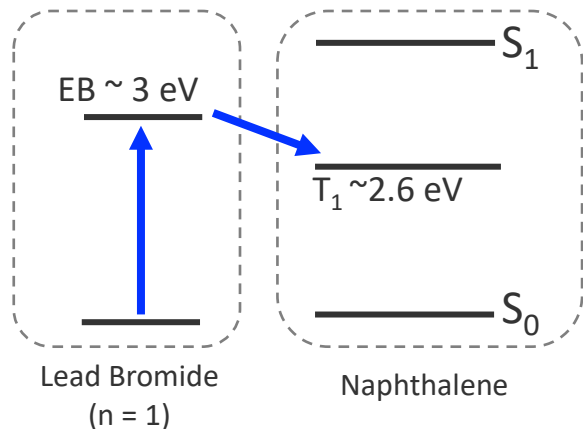
A heterojunction between lead bromide and naphthalene allows triplet energy transfer



1-naphthyl methylamine

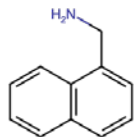


1-(2-naphthyl)methylamine

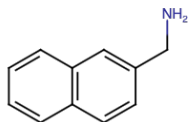


Naphthalene-based Ruddlesden-Popper perovskite

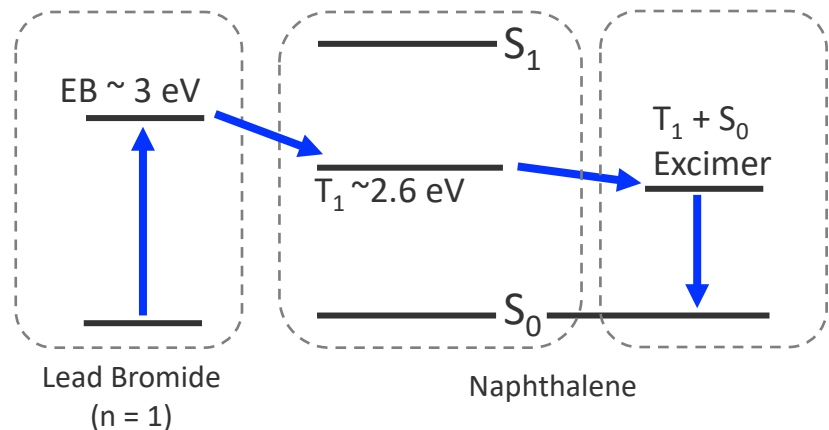
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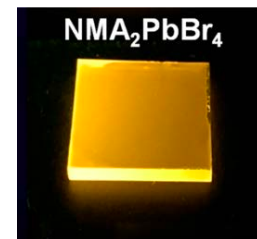
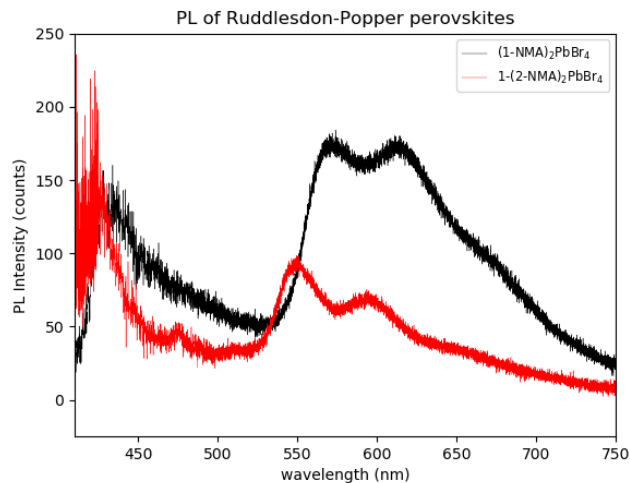
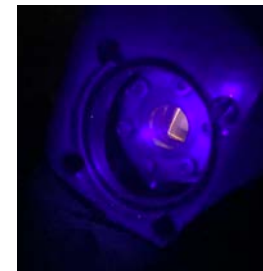
1-naphthyl methylamine



1-(2-naphthyl)methylamine

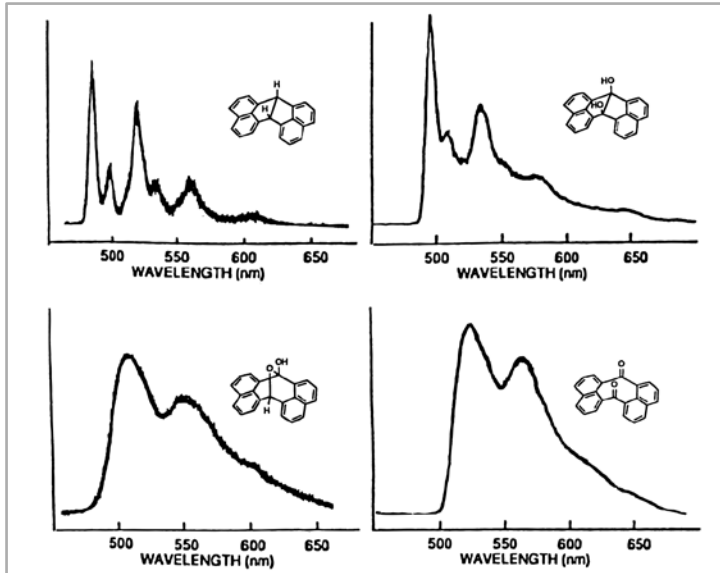


- Strong room temperature luminescence
- Photoluminescence is dominated by naphthalene *excimer* emission



Y. Tian *et al*, J. Phys. Chem. Lett. 11, 2247 (2020)

Excimer formation is orientation-dependent



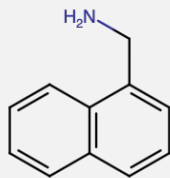
M. Terazima *et al*, J. Phys. Chem. A, 104, 1662 (2000)

A study on L-shaped naphthalene dimers showed that monomer vs. excimer phosphorescence was sensitive to:

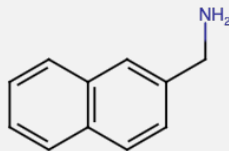
- Rigidity of the dimer
- Tilt angle of the dimer

RP vs. DJ: Structure & Properties

Ruddlesden-Popper

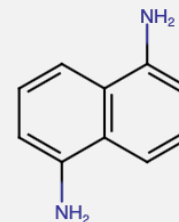


1-naphthyl methylamine



1-(2-naphthyl)methylamine

Dion-Jacobson



1,5-diamino naphthalene

Packing
geometry

Double layer of cations
Presumably strong pi-pi interactions

Single layer of cations
Reduced intermolecular
interaction?

Rigidity

Single ammonium tethers
Flexible organic layer

Tethered on both ends
More rigid organic layer?

Optical
properties

PL dominated by T_1S_0 excimer emission

Monomer
phosphorescence?

Dion-Jacobson structure: (1,5-NDA) PbBr₄

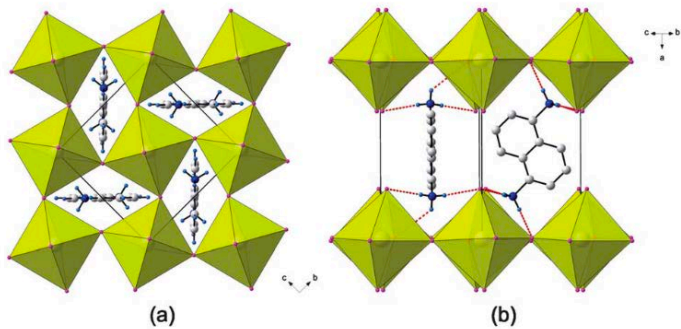


Fig. 7 (a) The 1,5-diammoniumnaphthalene molecules are almost perpendicular to each other. (b) The terminal halogen configuration and tilts of the fused rings.

A. Lemmerer and D. Billing, *Cryst. Eng. Comm.*, 14, 1954 (2012)

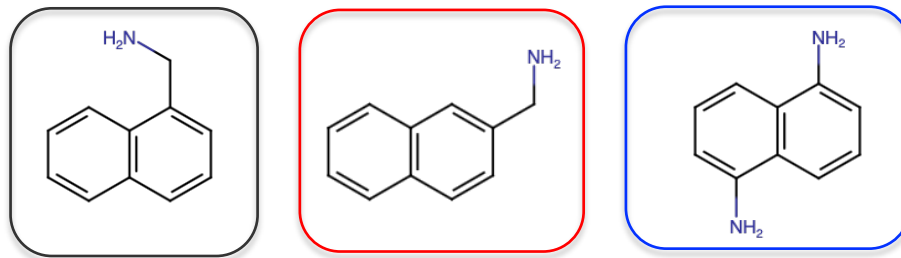
Crystal structure of iodide analogue shows:

- Naphthalene chromophores are *perpendicular* to each other
- Very little electronic interaction between pi-orbitals of neighboring naphthalenes

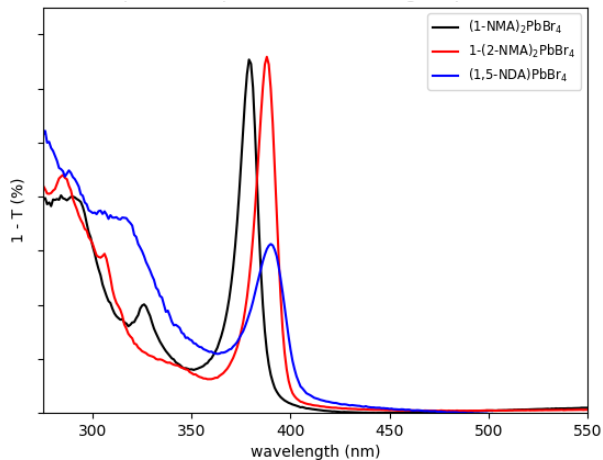
Hypotheses:

- Excimeric interactions in the DJ structure will be suppressed
- Material will exhibit triplet *monomer* phosphorescence rather than *excimer* emission

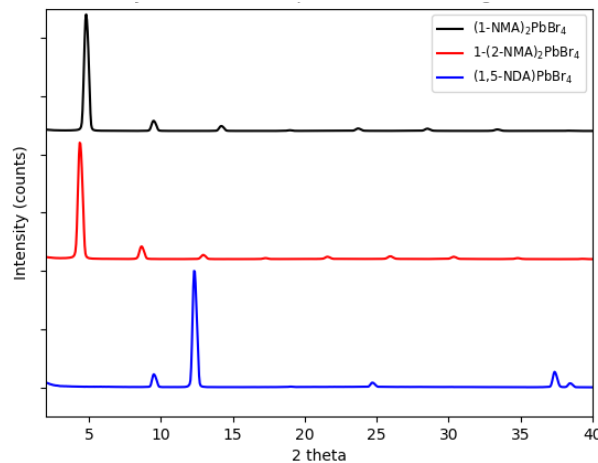
Absorption, XRD, and PL of naphthalene-containing 2D perovskites



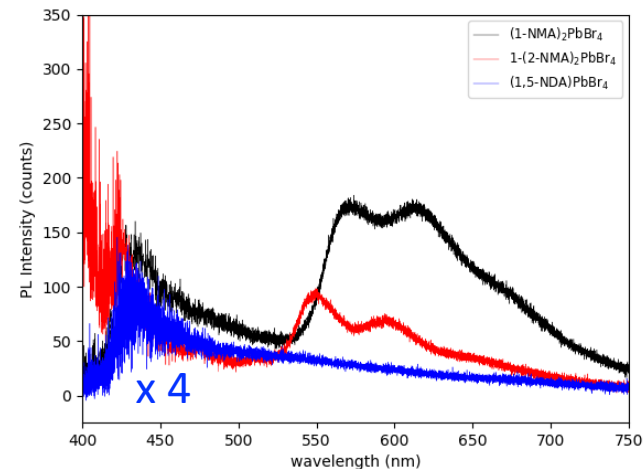
Absorbance



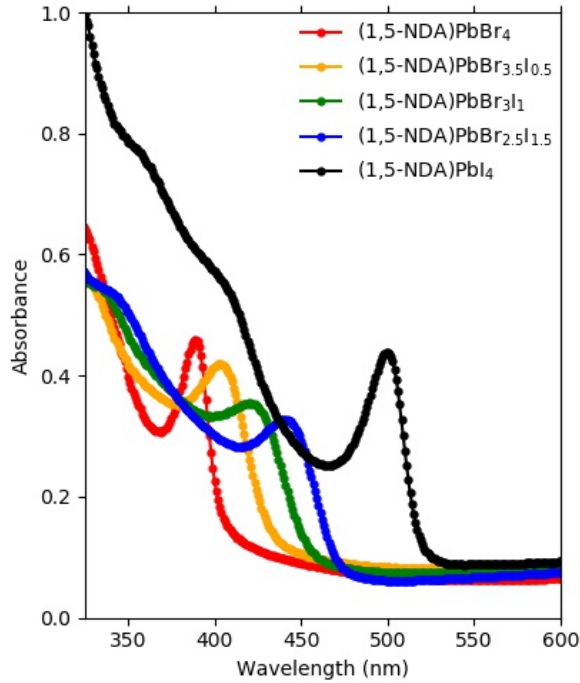
X-Ray Diffraction



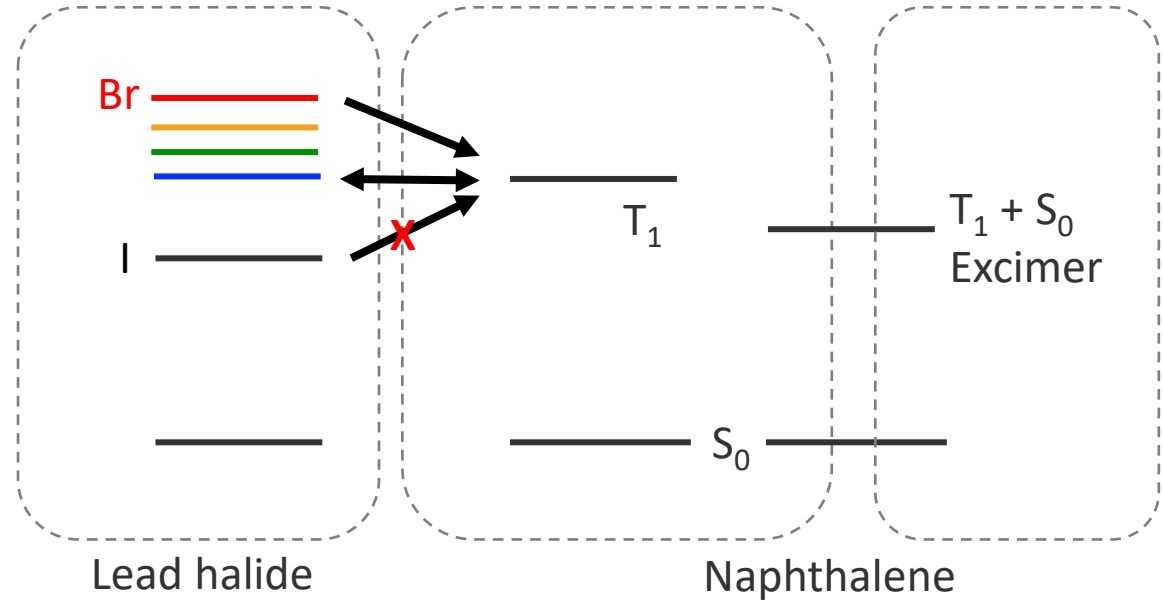
Photoluminescence



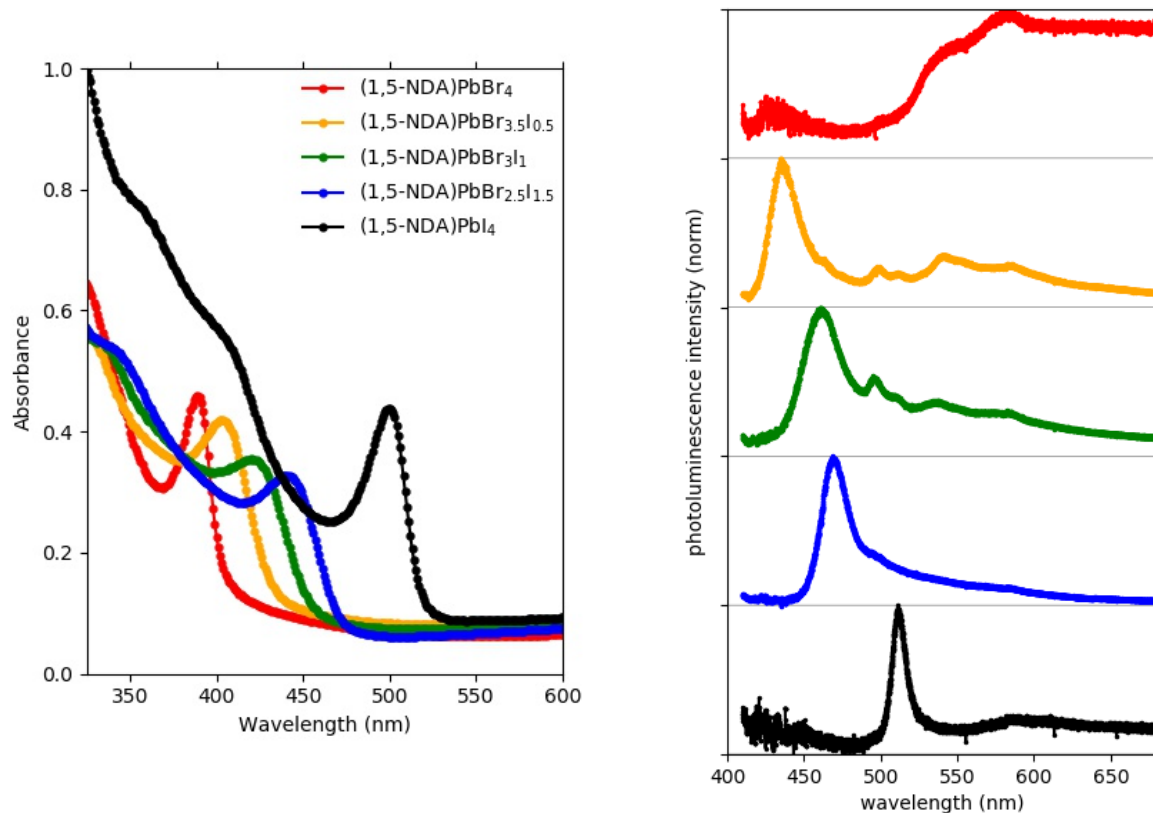
Heterojunction tuning by halide-mixing



Driving force for triplet energy transfer can be tuned by halide composition



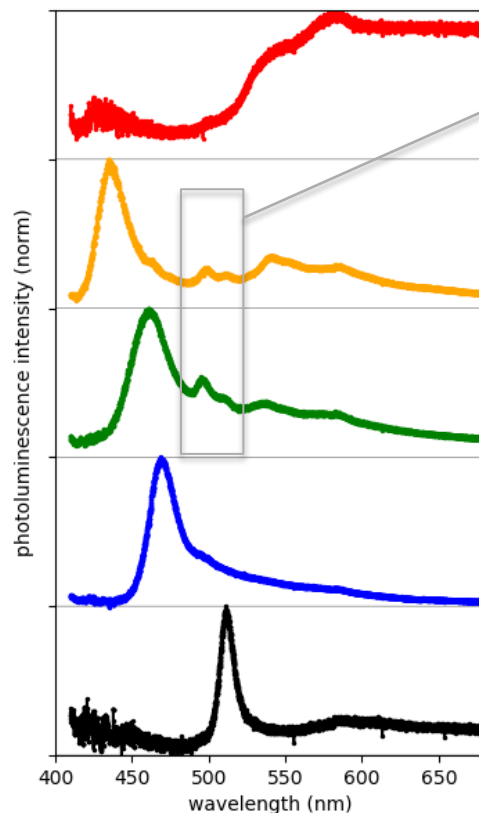
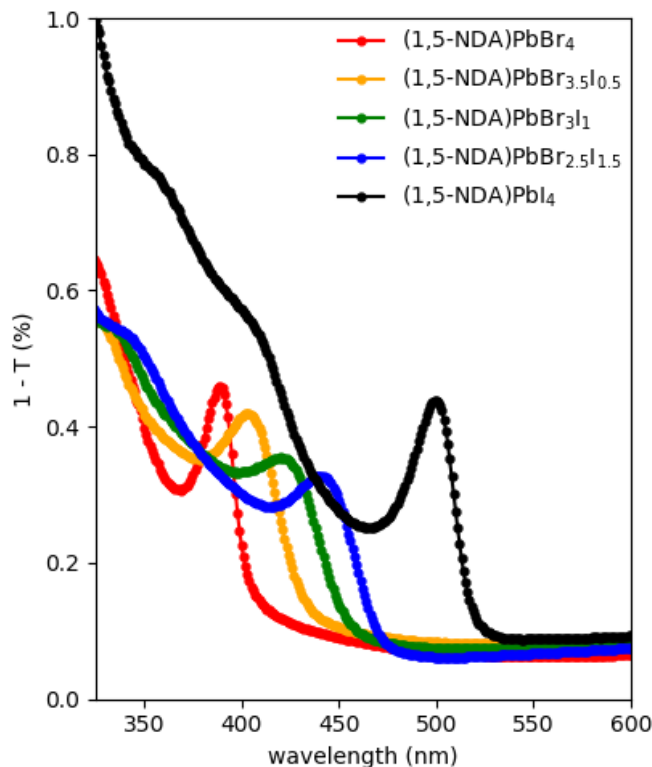
PL of mixed-halide compounds reflects driving force of triplet energy transfer



Composition	ΔE for TET
Br ₄	0.36 eV
Br _{3.5} I _{0.5}	0.32 eV
Br ₃ I ₁	0.17 eV
Br _{2.5} I _{1.5}	0.09 eV
I ₄	-0.18 eV

(Measured at 77 K)

PL of mixed-halide compounds reflects driving force of triplet energy transfer



(Measured at 77 K)

Extra peaks @495/510 nm?

- Sharp and closely spaced
- Unlikely to originate from the excimer

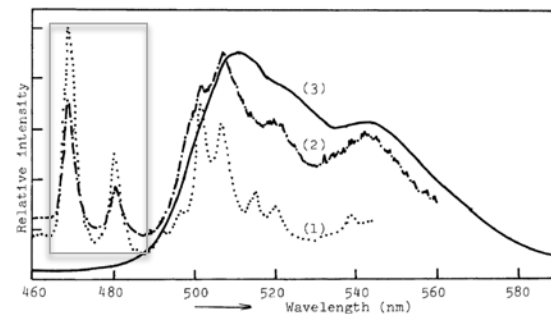
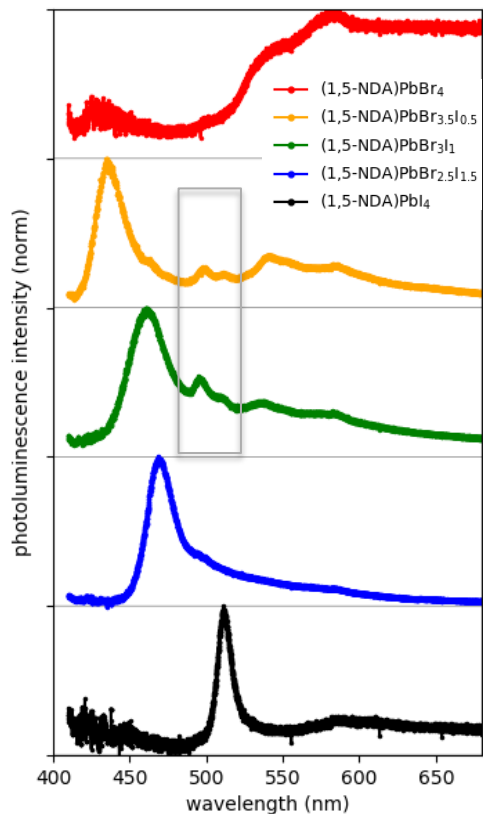


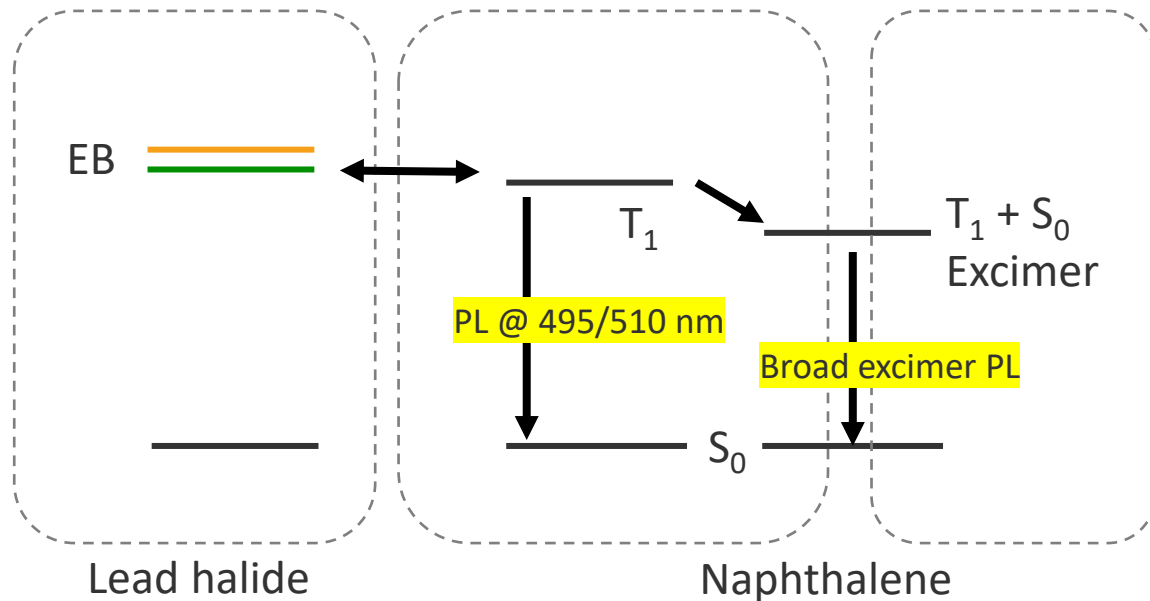
Fig. 1. Phosphorescence spectra for 1.5×10^{-4} M naphthalene solution in isoctane at different temperatures. (1) 77K; (2) 166K; (3) room temperature.

T. Takemura *et al*, Chem. Lett. 3, 1091 (1974)

Intermediate Br-I compositions show reversible triplet energy transfer



(Measured at 77 K)



Reversible triplet energy transfer at the PbX/naphthalene interface allows naphthalene *monomer phosphorescence* to compete with naphthalene *excimer formation*

Similar behavior reported in Ruddlesden-Popper perovskite

N. Kawano *et al*, J. Phys. Chem. C, 116, 22992 (2012)

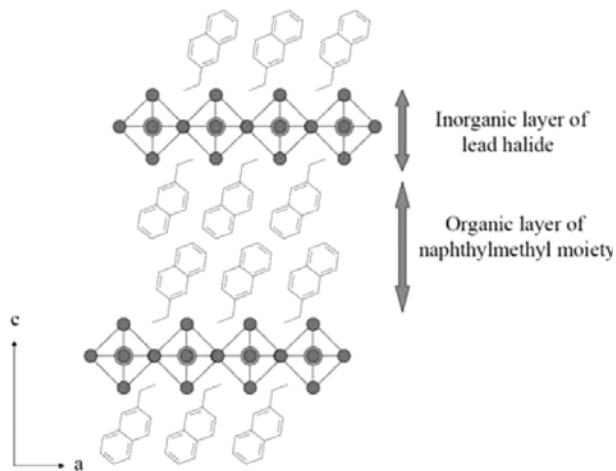
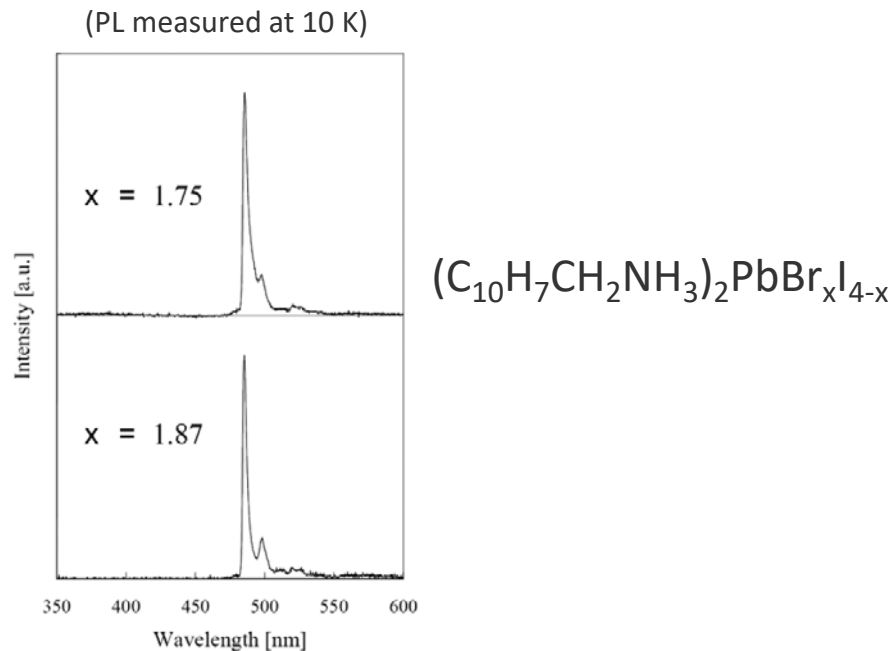
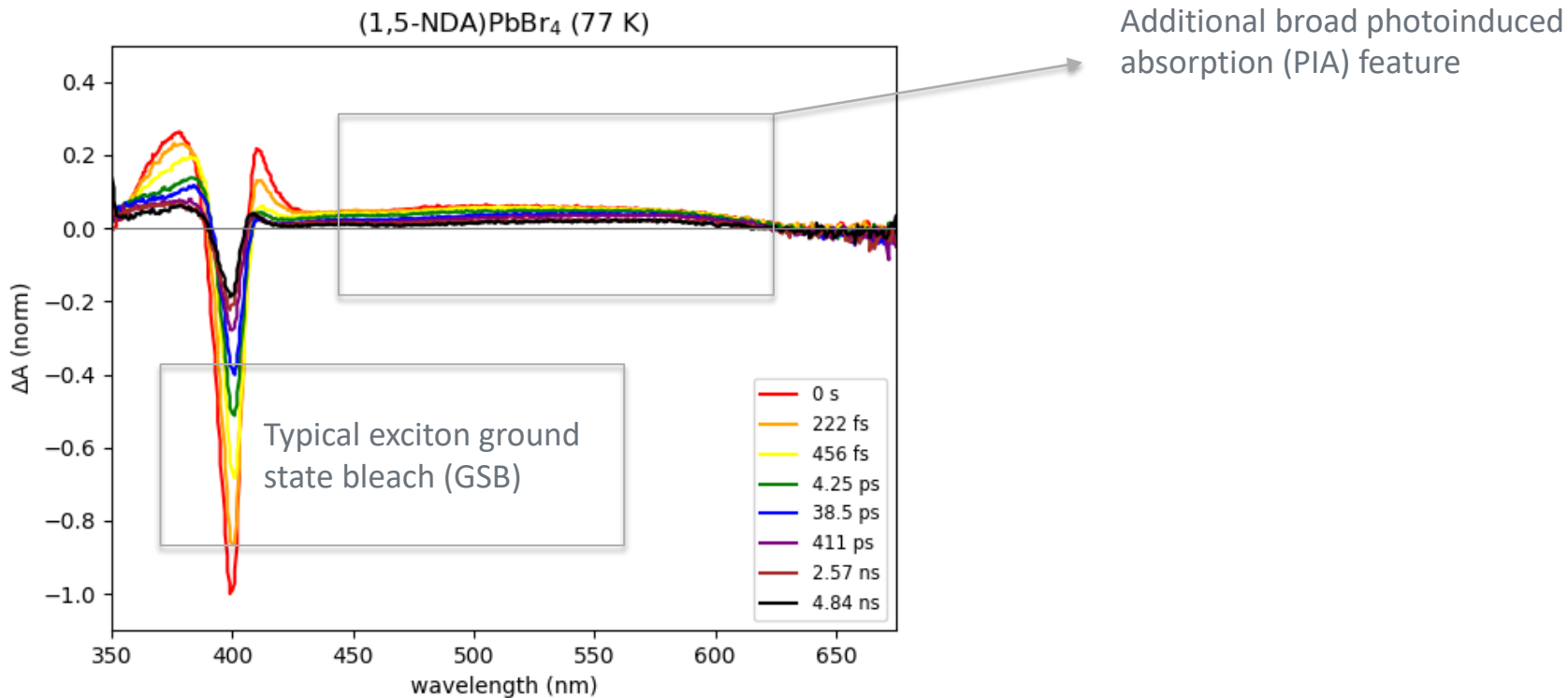


Figure 1. Schematic structure of metal halide-based layered perovskite with naphthylmethyl moieties.

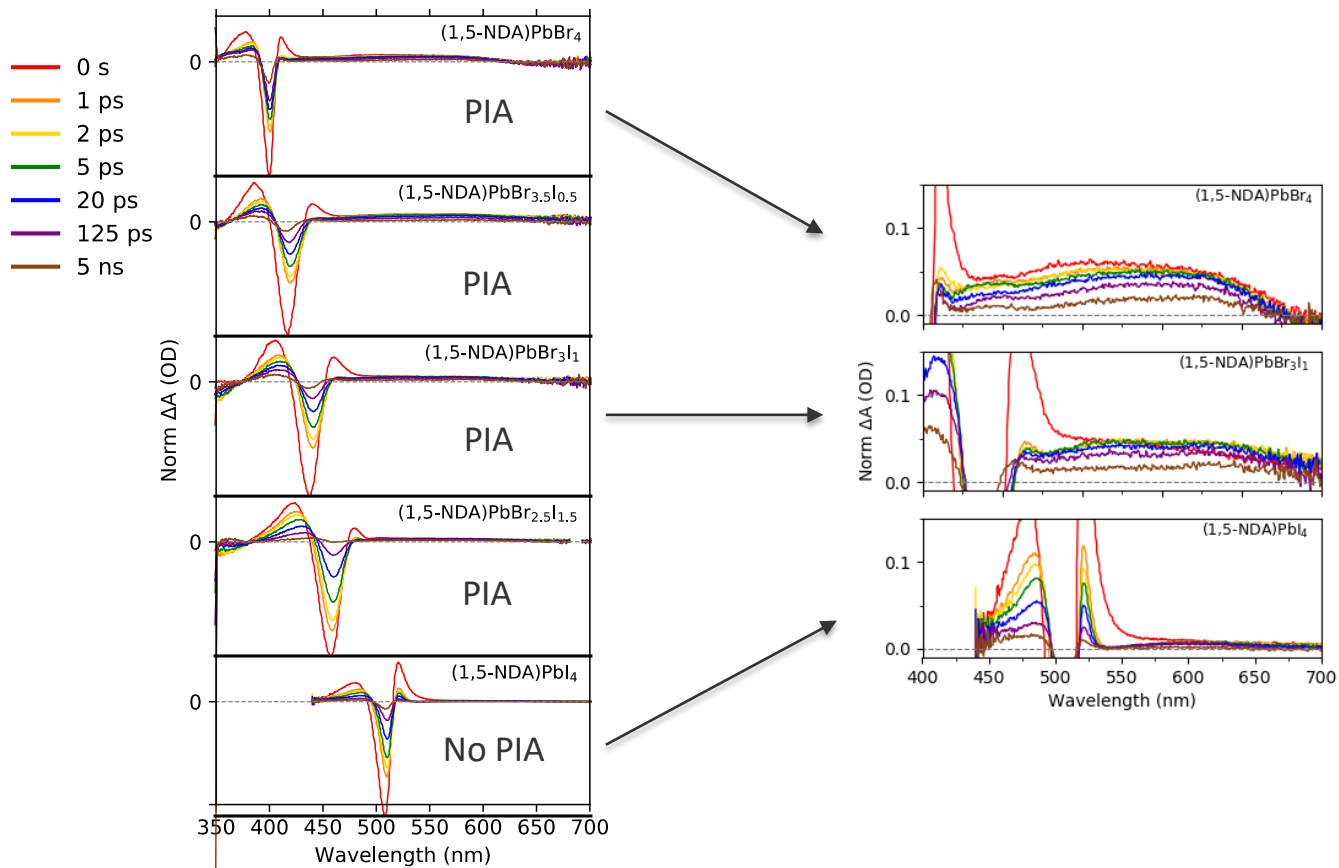


Radiative relaxation from the naphthalene triplet monomer was enhanced by hybridization of the inorganic and organic exciton levels

Ultrafast transient absorption spectroscopy as a probe of interfacial dynamics



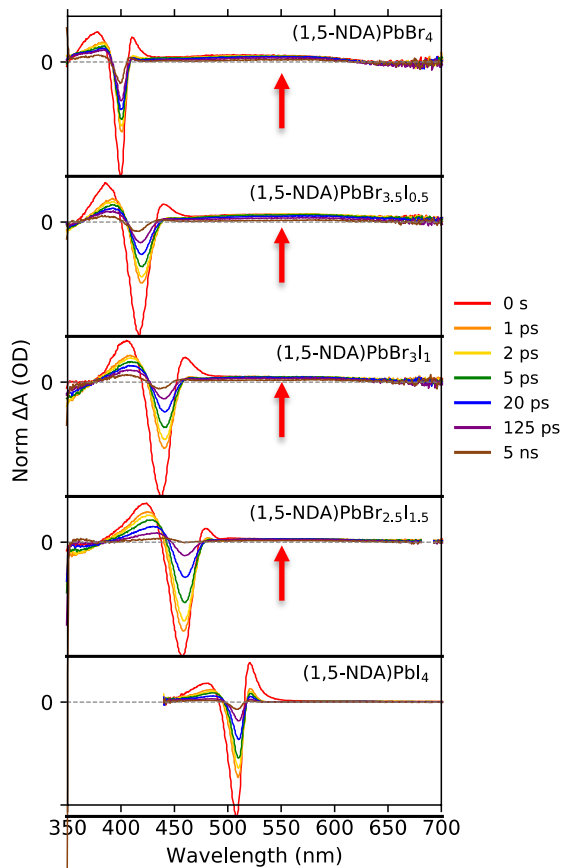
Presence of broad PIA is correlated with triplet energy transfer



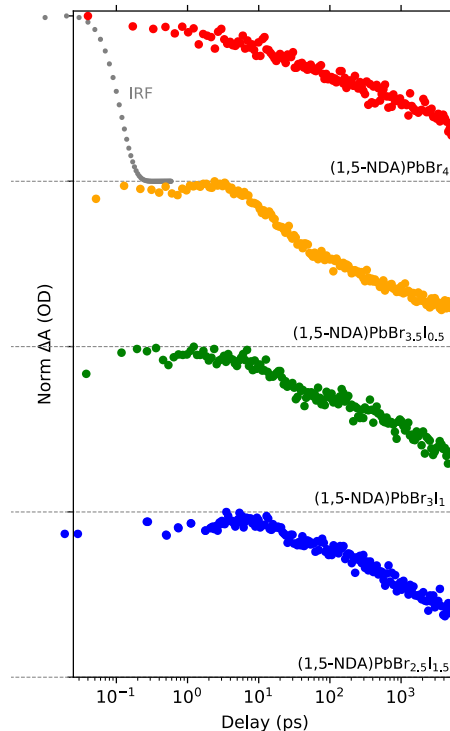
Kinetics of triplet formation is correlated with energetic driving force

Br_4 : large driving force for TET

$\text{Br}_{2.5}\text{I}_{1.5}$: small driving force for TET



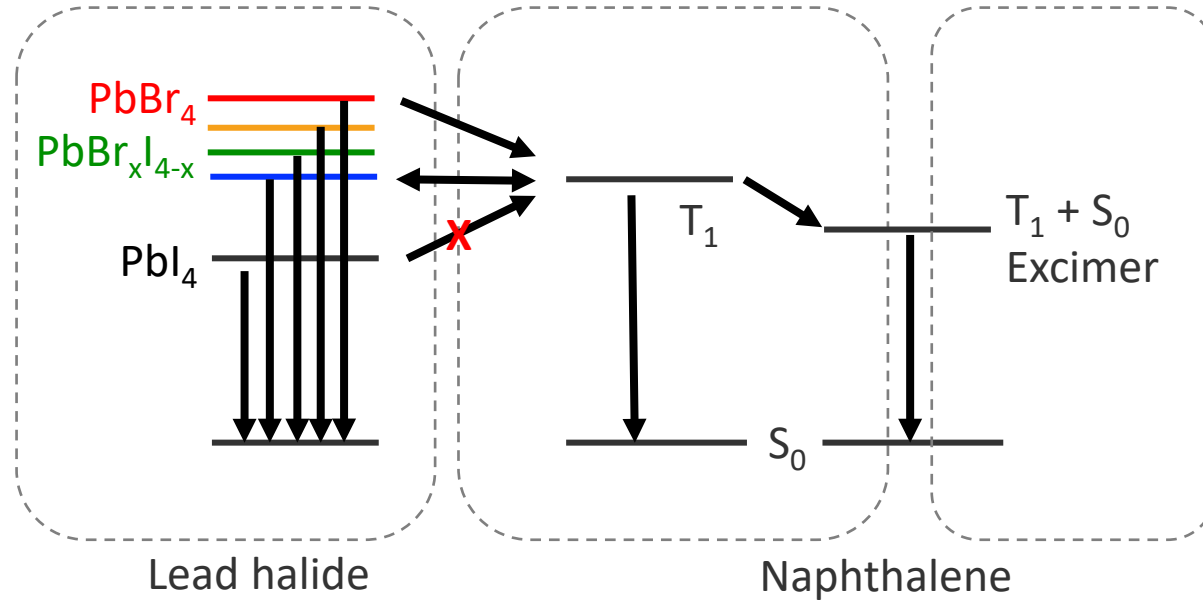
Kinetic Traces of PIA feature at 550 nm probe wavelength



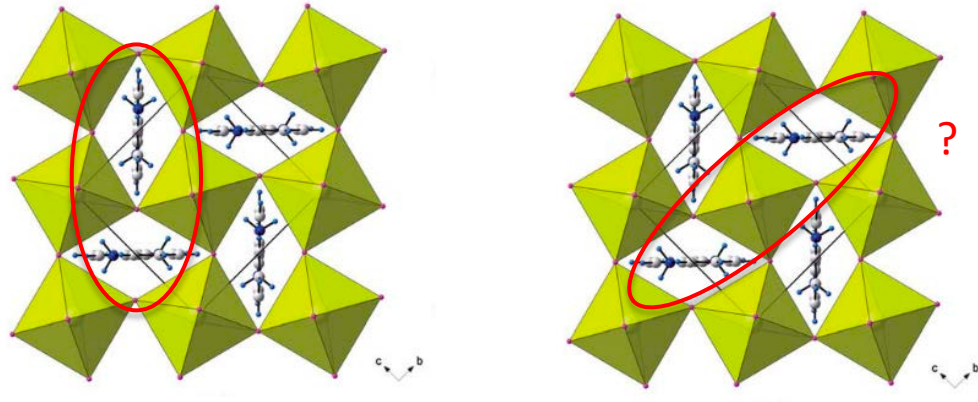
For large driving force, PIA maximum occurs within instrument response (170 fs)

For lower driving forces, PIA reaches maximum amplitude at a slight delay around 1-10 ps

Photophysical Picture



Excimers come in all shapes and forms...



A. Lemmerer and D. Billing, Cryst. Eng. Comm., 14, 1954 (2012)

Possible explanation: excimer could originate from *diagonal* pairs of naphthalenes arranged in a slipped-parallel fashion

For more information:

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Interlayer Triplet Energy Transfer in Dion–Jacobson Two-Dimensional Lead Halide Perovskites Containing Naphthalene Diammonium Cations

YunHui L. Lin and Justin C. Johnson*

Cite This: *J. Phys. Chem. Lett.* 2021, 12, 4793–4798 [Read Online](#)

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ABSTRACT: Recently, hybrid perovskites have gained attention as sensitizers for molecular triplet generation. Layered, two-dimensional (2D) perovskites are especially well-suited for this purpose because the triplet donor (inorganic framework) and triplet acceptor (organic layer) are self-assembled into adjacent sheets, so that with the appropriate energetics, triplets can be driven across the interface. Here we examine interlayer energy transfer in a series of mixed-halide Dion–Jacobson 2D perovskites containing divalent naphthalene cations. We find that the sensitized phosphorescence in these compounds is dominated by naphthalene triplet excimer emission, but when the inorganic exciton is tuned near resonance with the naphthalene triplet, naphthalene monomer phosphorescence competes with triplet excimer formation. The interlayer energy-transfer process is further revealed by ultrafast transient absorption spectroscopy through kinetic variations in triplet excimer formation times. Ultimately, gaining control over interlayer interactions in 2D perovskites through cation design will help uncover new functions and applications for these materials.

Dion-Jacobson phase

Lead halide: $PbBr_2$, $PbdBr_2$, Pbl_2

Naphthalene: T_1 , S_0 , $T_1 + S_0$ Excimer

Email: yunhui.lin@nrel.gov

Thank you

Mentor: Justin C. Johnson

Funding: NREL Laboratory Directed R&D Program

US DOE Basic Energy Sciences, Solar Photochemistry Program

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