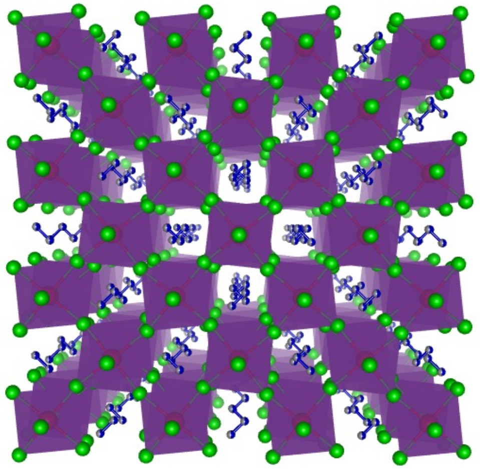
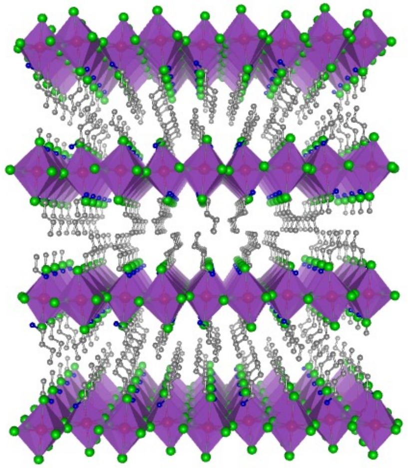
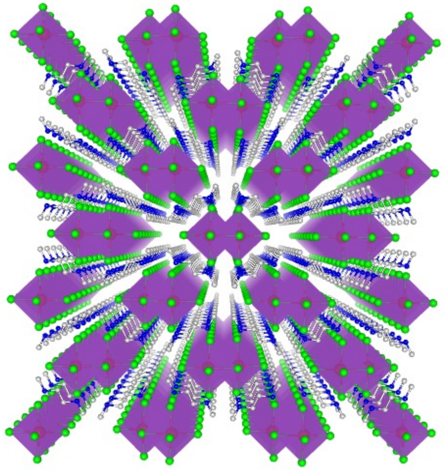
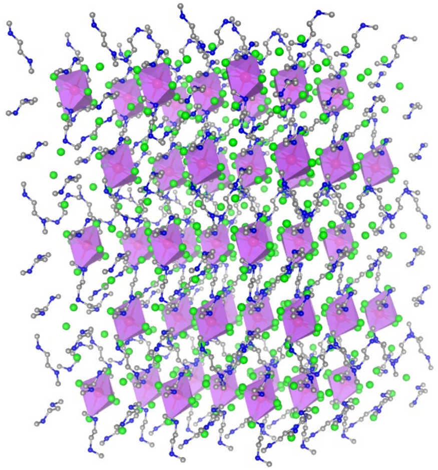
Low Dimensional Metal Halide Perovskites and Hybrids:

From Synthetic Control to Device Integration

Biwu Ma

Department of Chemistry and Biochemistry

Materials Science and Engineering Program (Affiliated)

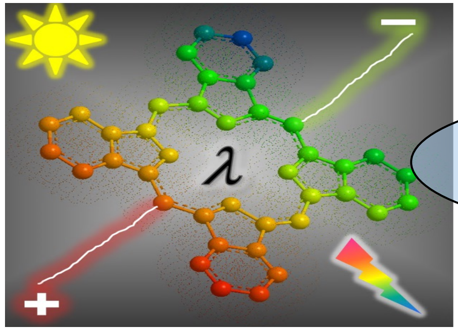
Florida State University

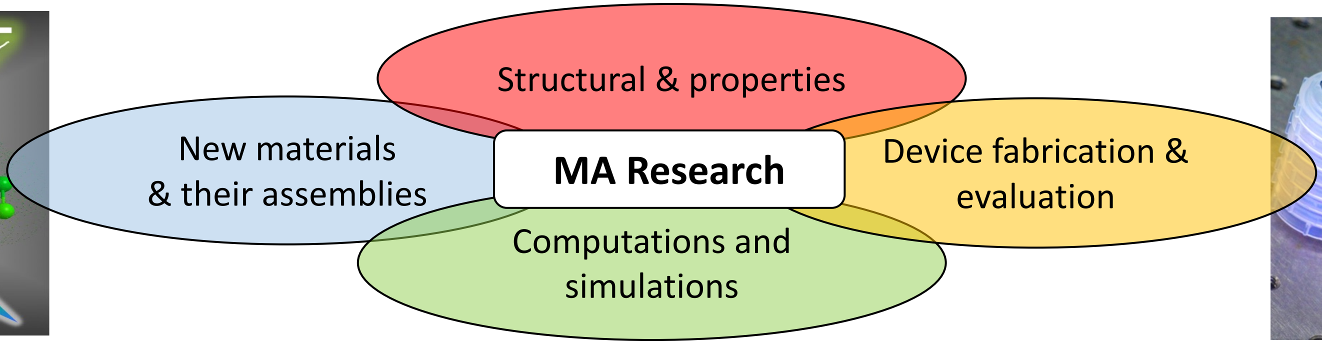
MA • GROUP

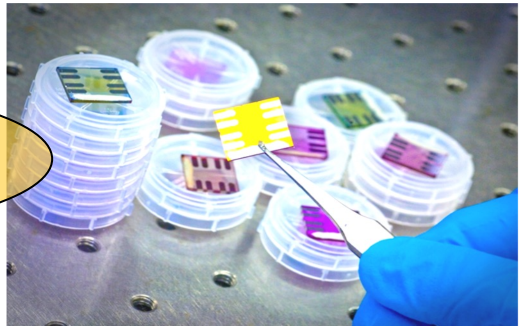
Advanced Materials for Electronic & Energy Devices

FLORIDA STATE UNIVERSITY 1851

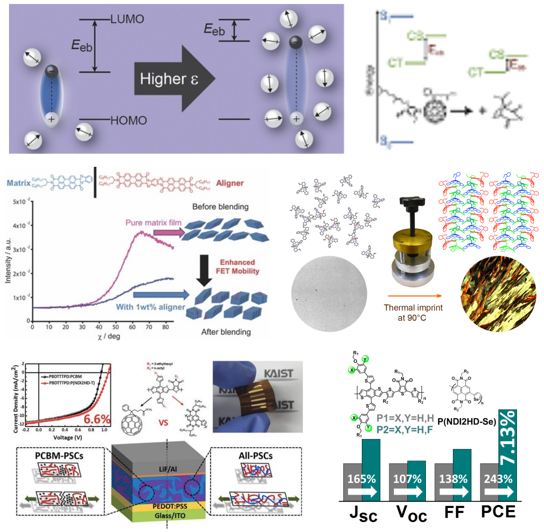
Ma Group @ FSU





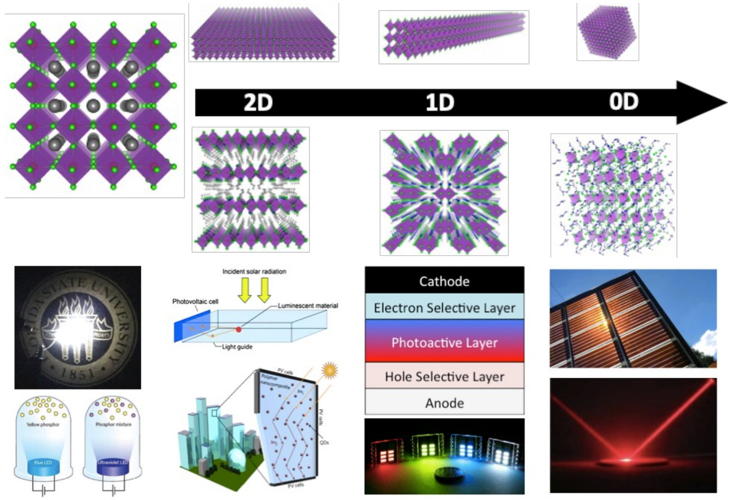


Organic Electronics



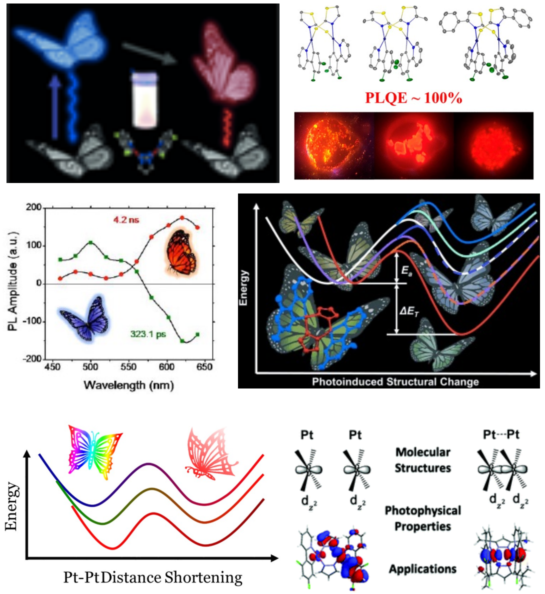
ACS Appl. Mater. Interfaces, **2013**, *5*, 10105-10110; *Advanced Functional Materials*, **2014**, *24*, 7588-7596; **2017**, *27*, 1703070; **2020**, *30*, 2005787; *The Journal of Physical Chemistry C*, **2017**, 121, 3279-3285. *Advanced Materials*, **2014**, *26*, 1223-1228; **2016**, *28*, 10016–10023; *Advanced Materials Interfaces*, **2016**, 3, 1600179; *Journal of Vacuum Science & Technology B*, **2017**, 35, 06G801; *Nature Communications*, **2015**, *6*, 8547

Metal Halide Perovskites and Beyond



Science Advances, **2020**, 6, eaaz5961; *Nature Communications*, **2017**, *8*, 14051; **2020**, *11*, 4329; *JACS*, **2018**, *140*, 13181-13184; **2020**, *142*, 16001-16006; *Angew. Chem. Int. Ed.*, **2017**, 56, 9018-9022; **2018**, 57, 1021-1024; **2020**, *59*, 14120-14123; **2020**, *59*, 23067-23071; **2021**, *133*, 2515-2522; *Advanced Materials*, **2016**, 28, 305-311; **2016**, *28*, 8983-8989 **2018**, *30*, 1707093; *ACS Energy Letters*, **2018**, *3*, 54-62; **2018**, *3*, 1443-1449; **2019**, *4*, 1579-1583; *Chemical Science*, **2017**, 8, 8400-8404; **2018**, 9, 586-593; *ACS Materials Letters*, **2019**, *1*, 594-498; **2020**, *2*, 376-380; **2020**, *2*, 633-638; *J. Phys. Chem. Lett.* **2018**, *9*, 2164-2169; **2019**, *10*, 5836–5840; **2019**, *10*, 5923–5928; **2021**, *12*, 8229–8236; *Materials Science & Engineering R*, **2019**, *137*, 38-65; *Advanced Optical Materials*, **2019**, *7*, 1801474; **2020**, *9*, 2001766; *Chemistry of Materials*, **2018**, *30*, 2374-2378; **2020**, *32*, 374-380

Molecular Photochemistry

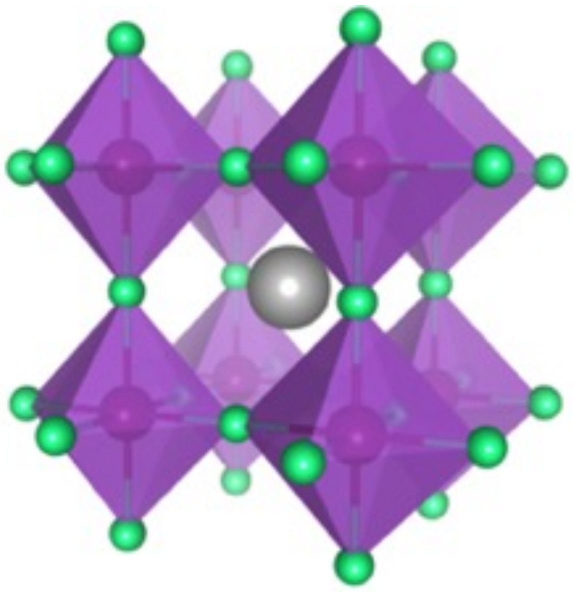


Angew. Chem. Int. Ed., **2014**, *53*, 10908-10912; **2015**, *54*, 9591-9595; *Inorg. Chem*, **2016**, *55*, 8564-8569; **2020**, *59*, 13109-13116; *Chemistry - A European Journal*, **2017**, 23, 1-7; *J. Mater. Chem. C*, **2019**, *7*, 5910—5924

Outline

- **Metal Halide Perovskites**
  - Molecular View of Metal Halide Perovskites
  - Perovskite Solar Cells
  - Electrically Driven LEDs
- **Organic Metal Halide Hybrids Beyond Perovskites**
  - From 3D to 2D, 1D, and 0D
  - From Single-Component to Multi-Component Systems
  - Applications of Organic Metal Halide Hybrids
- **Conclusions**
- **Acknowledgement**

Metal Halide Perovskites



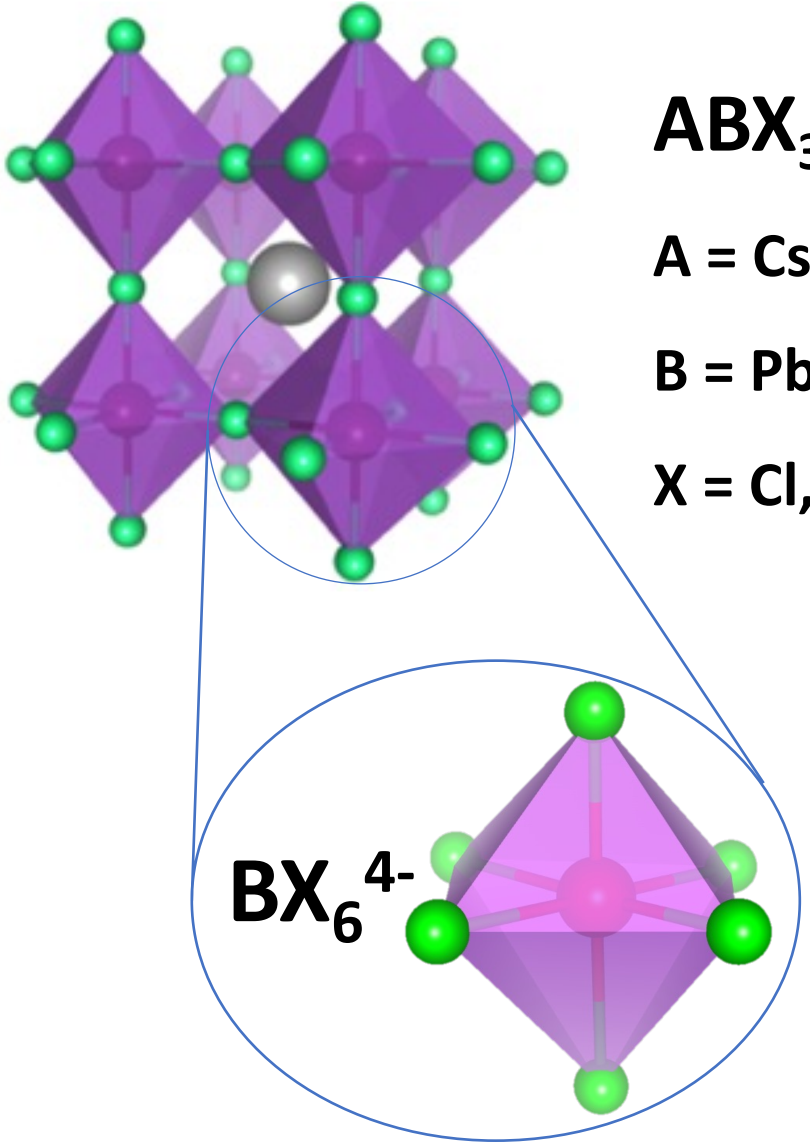
ABX_3

A = Cs, CH_3NH_3, etc.

B = Pb, Sn, etc.

X = Cl, Br, I

Metal Halide Perovskites



ABX_3

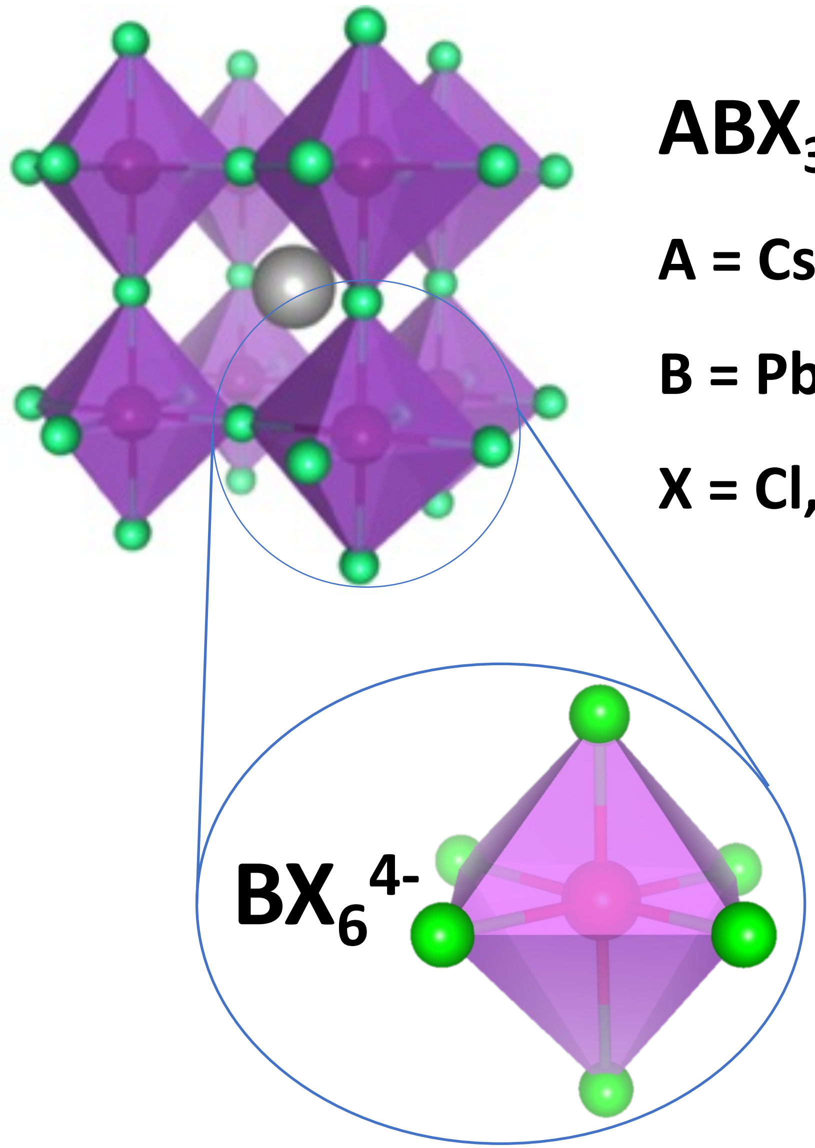
A = Cs, CH_3NH_3, etc.

B = Pb, Sn, etc.

X = Cl, Br, I

ACS Energy Letters, **2018**, *3*, 54-62; *Materials Research Letters*, **2018**, *6*, 552-569; *Materials Science & Engineering - R: Reports*, **2019**, *137*, 38-65; *Advanced Optical Materials*, **2021**, *9*, 2001766

Metal Halide Perovskites

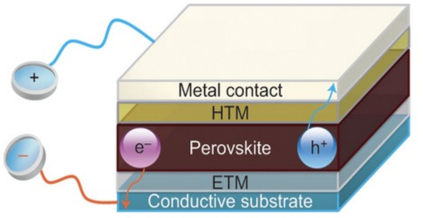


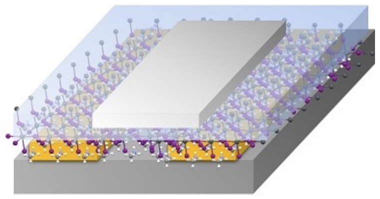
ABX_3

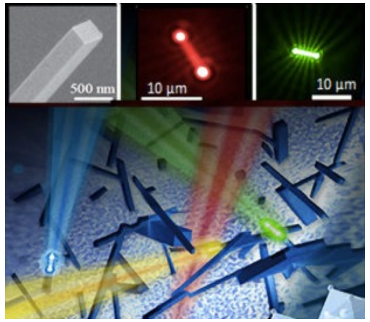
A = Cs, CH_3NH_3

B = Pb, Sn, etc.

X = Cl, Br, I



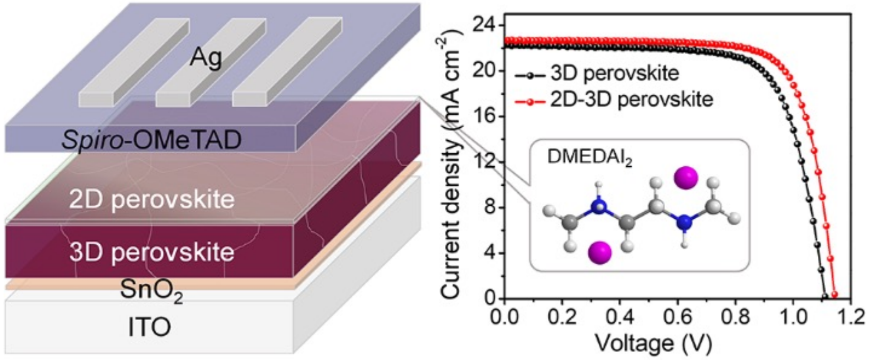




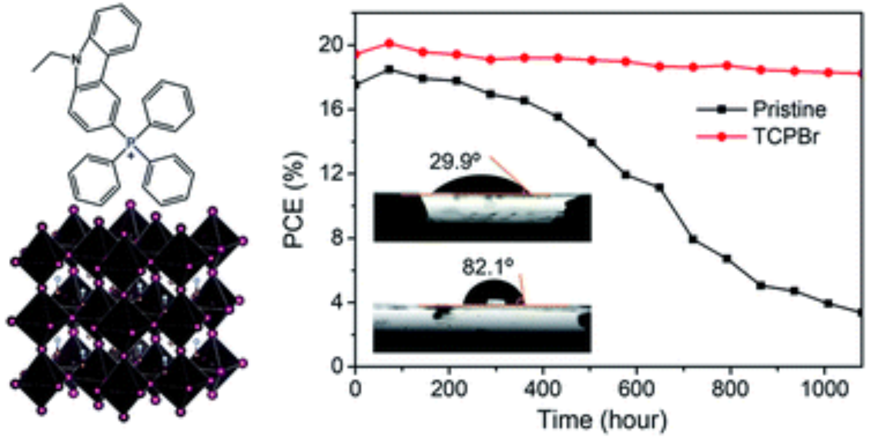
- **Solution Processable Semiconductors**
  - Low-cost, earth-abundant
  - Facile synthesis and preparation
  - Highly tunable band gaps
  - Exceptional charge transport
  - High absorption coefficients
  - Narrow emissions with high color purity
- **Issues and Challenges**
  - Low stability of materials and devices
  - Eco-friendly lead-free
  - Processing and patterning

ACS Energy Letters, **2018**, *3*, 54-62; *Materials Research Letters*, **2018**, *6*, 552-569; *Materials Science & Engineering - R: Reports*, **2019**, *137*, 38-65; *Advanced Optical Materials*, **2021**, *9*, 2001766

Perovskite Solar Cells



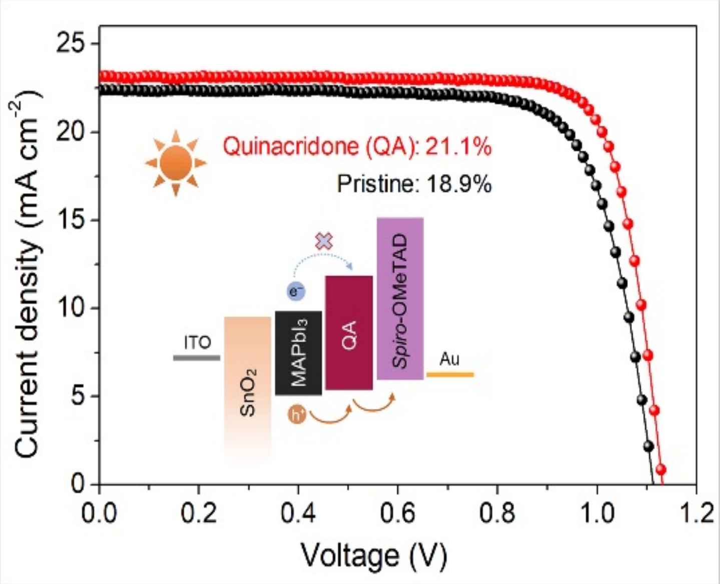
ACS Applied Materials and Interfaces, **2020**, 12, 1159-1168

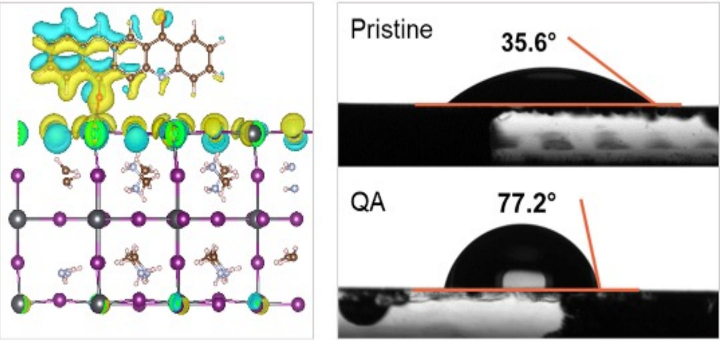


Journal of Materials Chemistry A, **2020**, *8*, 2039-2046

Surface Passivation:

Suppress charge recombination at the interfaces between halide perovskite and charge transport layers for high device efficiency and prevent the penetration of degrading agents into the perovskite layer for high device stability. Various materials have been employed to passivate perovskite thin films, including low-dimensional metal halides, alkaline and organic halides, polymers, inorganic compounds, and so on.



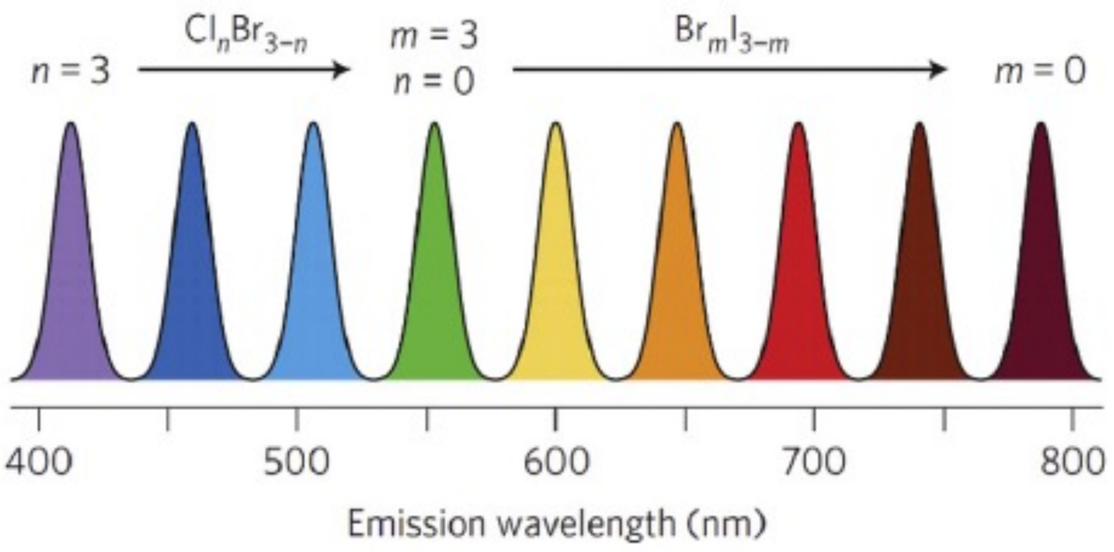


Angewandte Chemie, **2020**, *60*, 2485-2492

Color Tuning and Perovskite LEDs

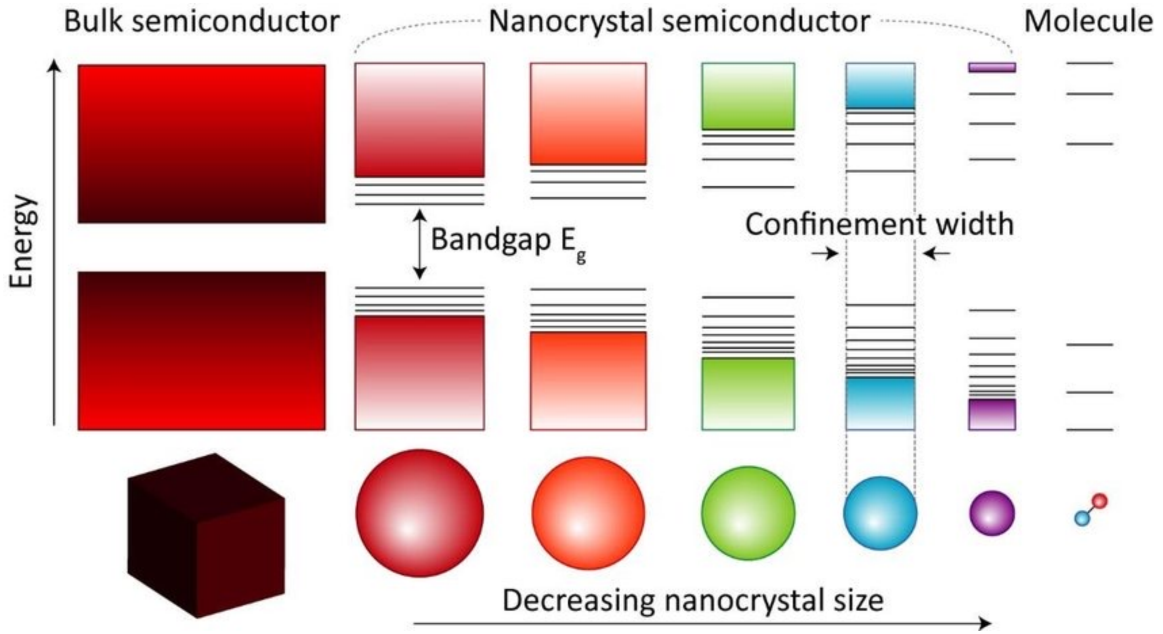
- Composition control, Quasi-2D, and Hollow nanostructures

Compositional Modulation



Nano Materials Science **2019**, *1*, 268–287

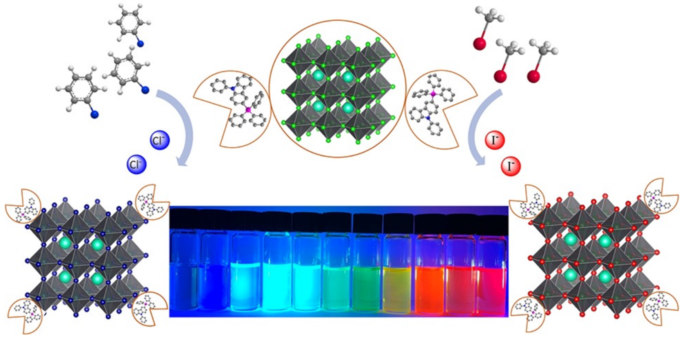
Quantum Size Effects



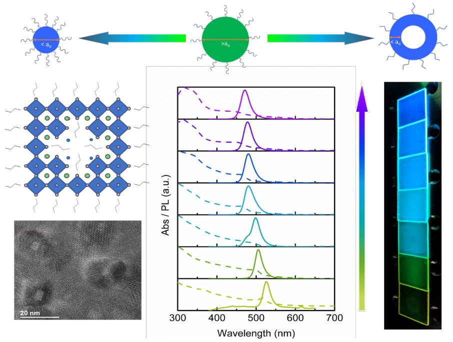
Topics in Current Chemistry **2016**, *374*, 58

Color Tuning and Perovskite LEDs

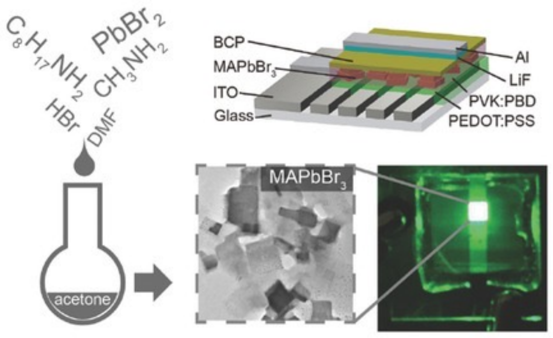
- Composition control, Quasi-2D, and Hollow nanostructures
- Perovskite LEDs via Bottom-up & Top-down approaches



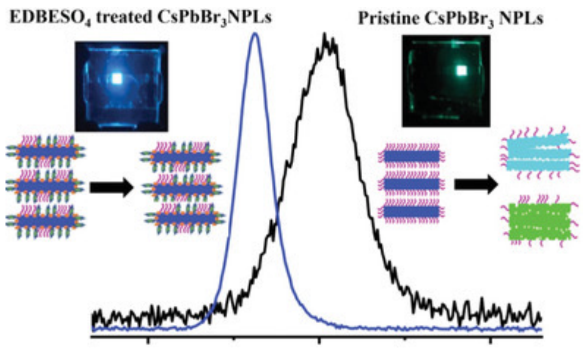
JPCL, **2019**, *10*, 5836–5840



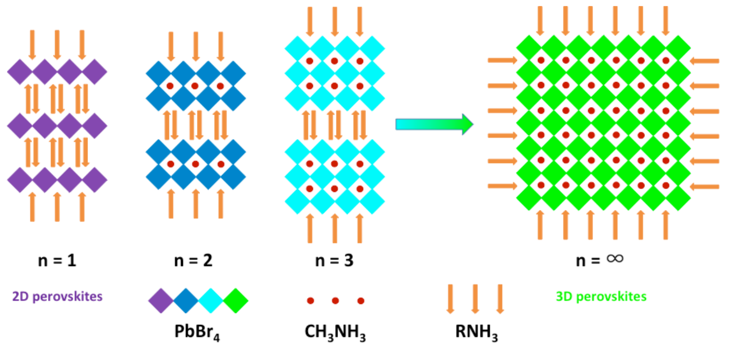
Science Advances, **2020**, *6*, eaaz5961



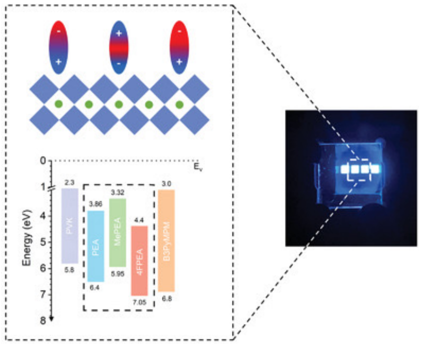
Advanced Materials **2016**, *28*, 305-311



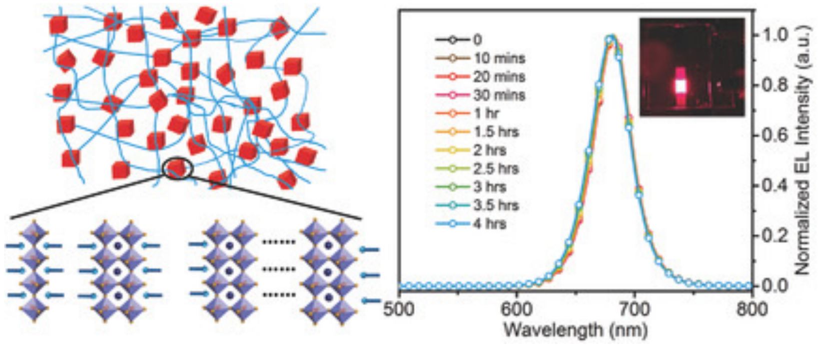
Advanced Energy Materials, **2022**, 2201605



Chemical Communications, **2016**, *52*, 3887-3890



Advanced Functional Materials, **2021**, *31*, 2103299



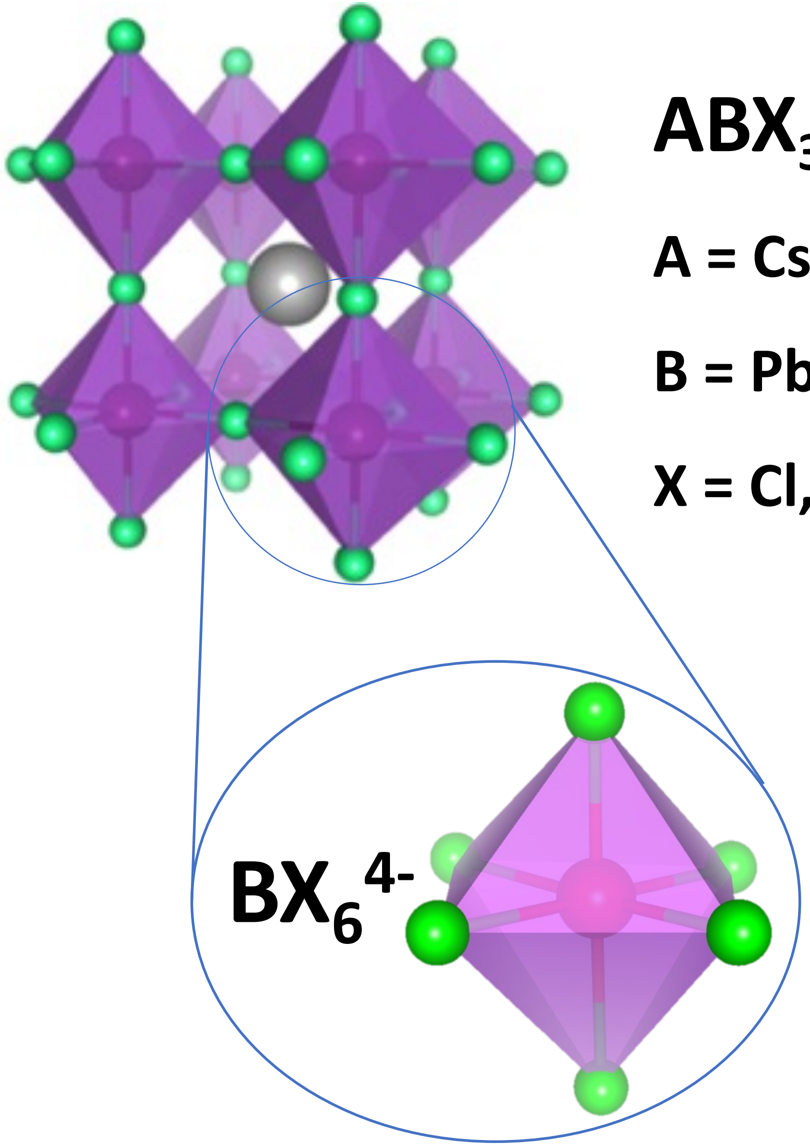
Advanced Materials, **2018**, *30*, 1707093

Small Science, **2021**, *1*, 2000072

Outline

- Metal Halide Perovskites
  - Molecular View of Metal Halide Perovskites
  - Perovskite Solar Cells
  - Electrically Driven LEDs
- **Organic Metal Halide Hybrids Beyond Perovskites**
  - From 3D to 2D, 1D, and 0D
  - From Single-Component to Multi-Component Systems
  - Applications of Organic Metal Halide Hybrids
- Conclusions
- Acknowledgement

Beyond Halide Perovskites

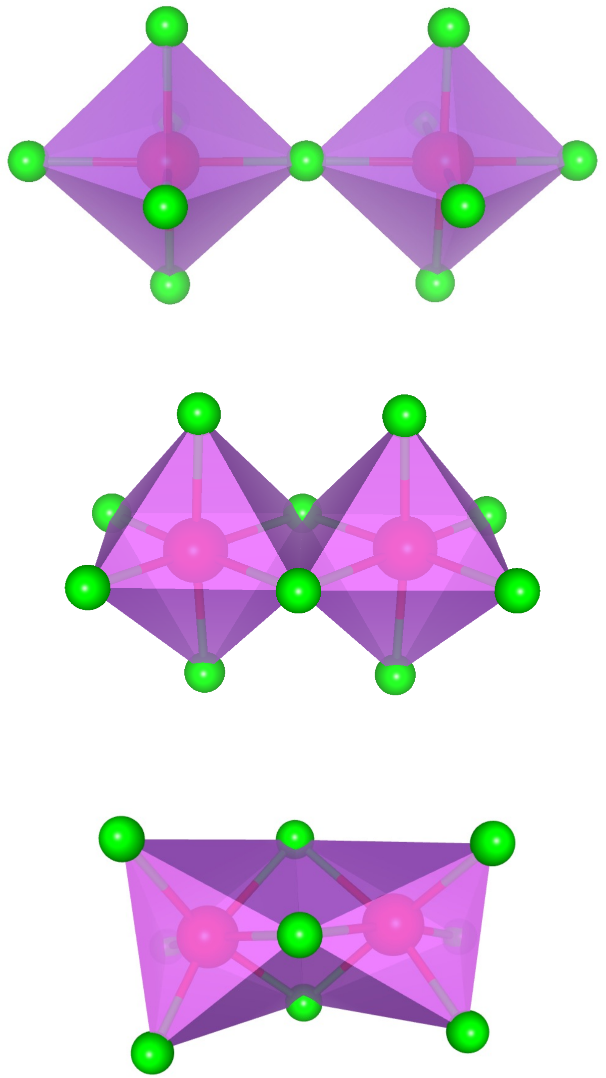


ABX_3

A = Cs, CH_3NH_3, etc.

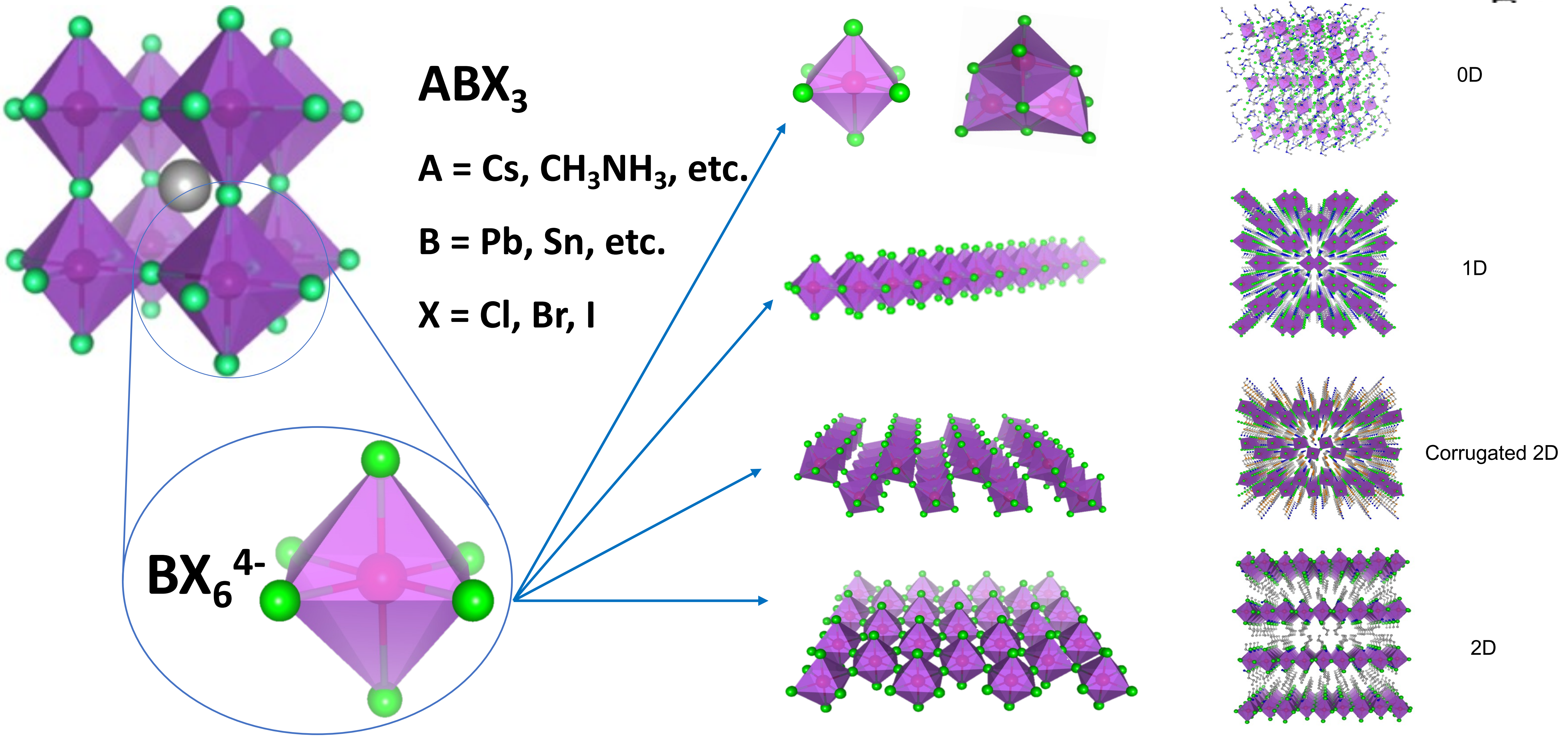
B = Pb, Sn, etc.

X = Cl, Br, I



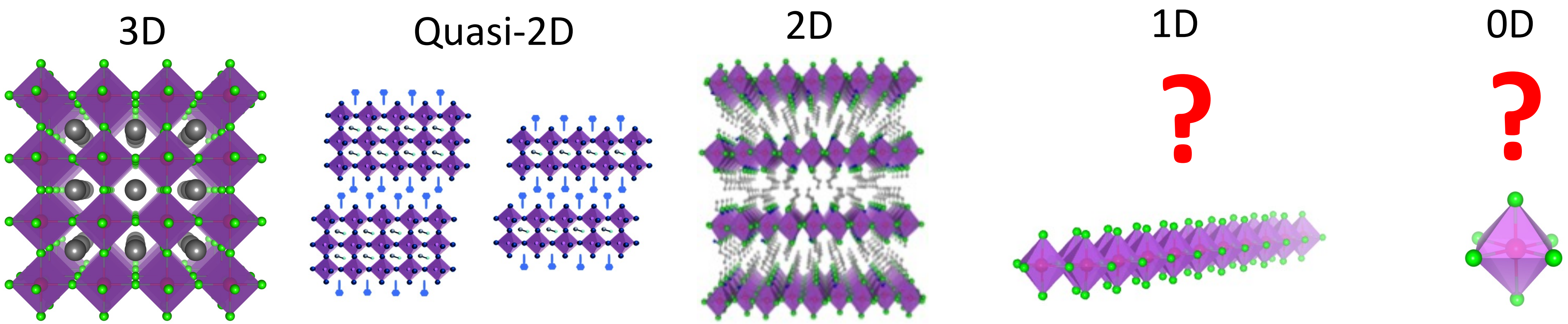
ACS Energy Letters, **2018**, *3*, 54-62; *Materials Research Letters*, **2018**, *6*, 552-569; *Materials Science & Engineering - R: Reports*, **2019**, *137*, 38-65; *Advanced Optical Materials*, **2021**, *9*, 2001766

Beyond Halide Perovskites

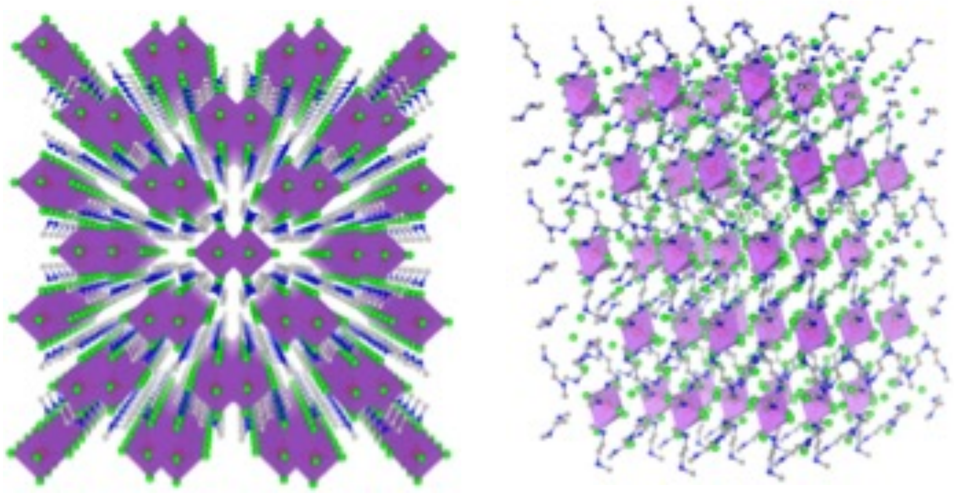


ACS Energy Letters, **2018**, *3*, 54-62; *Materials Research Letters*, **2018**, *6*, 552-569; *Materials Science & Engineering - R: Reports*, **2019**, *137*, 38-65; *Advanced Optical Materials*, **2021**, *9*, 2001766

Low Dimensional Structures



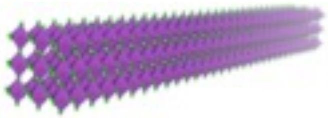
By choosing appropriate organic cations and metal halides, can the crystallographic structures of organic metal halide hybrids be finely controlled to exhibit different dimensionalities at the molecular level, with the metal halide octahedra forming zero- (0D), one- (1D), two- (2D), and three-dimensional (3D) structures?



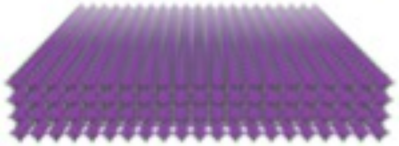
Low Dimensional Structures

MA·GROUP
Advanced Materials for Electronics & Energy Devices

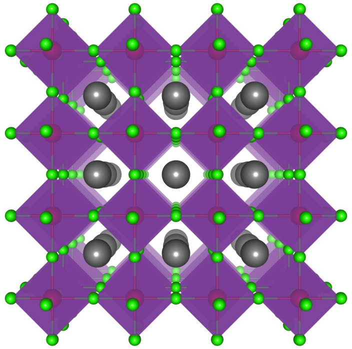
0D Quantum Dots



1D Nanowires

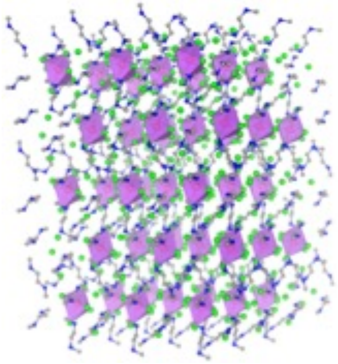


2D Nanoplatelets

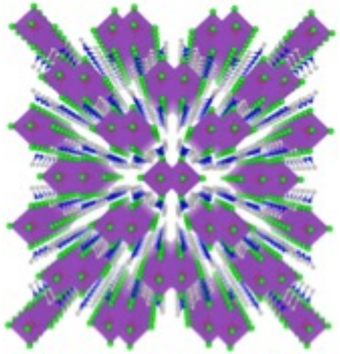


- ➢ **Morphological Low Dimensional Metal Halide Perovskites (Still 3D ABX_3)**
- ➢ **Molecular Level Low Dimensional Organic Metal Halide Hybrids**

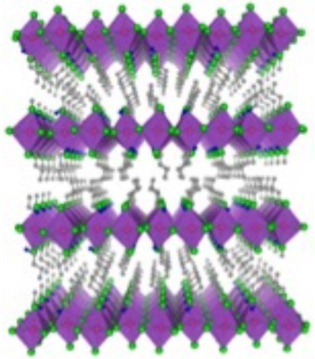
0D



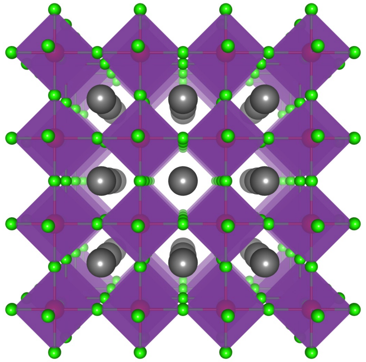
1D



2D

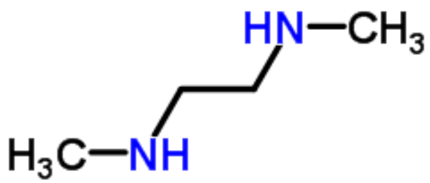


3D

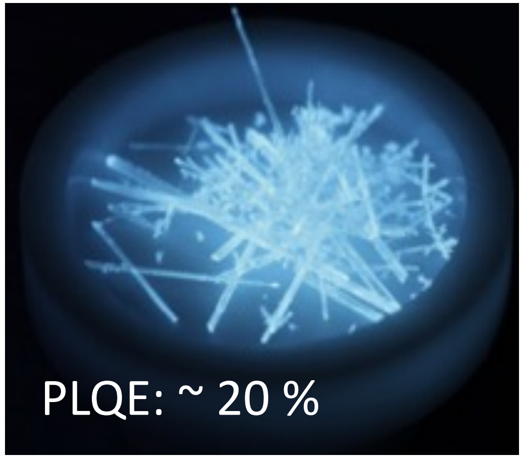


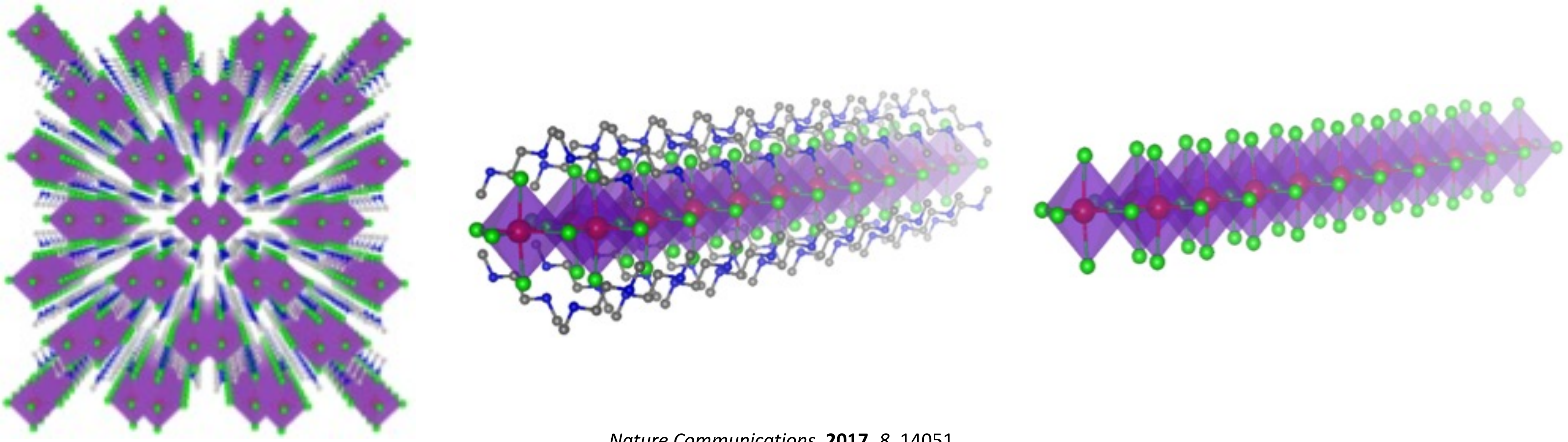
Single Crystalline Bulk Assemblies of Quantum Confined Materials

1D Organic Lead Bromide Hybrid



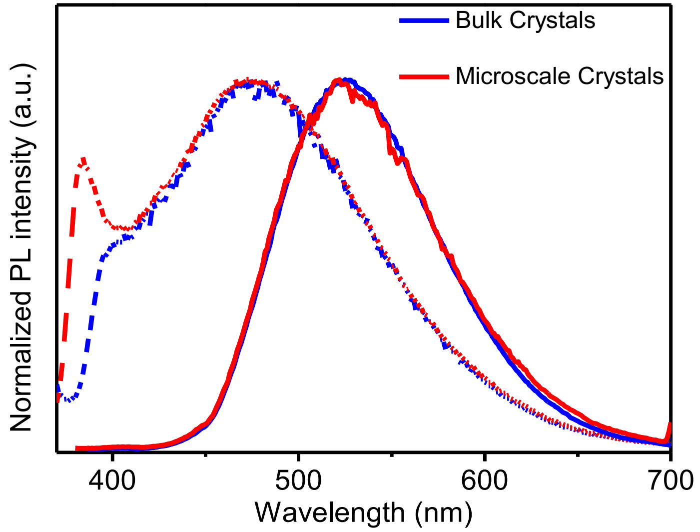
+ $2HBr$ + $PbBr_2$ ⟶

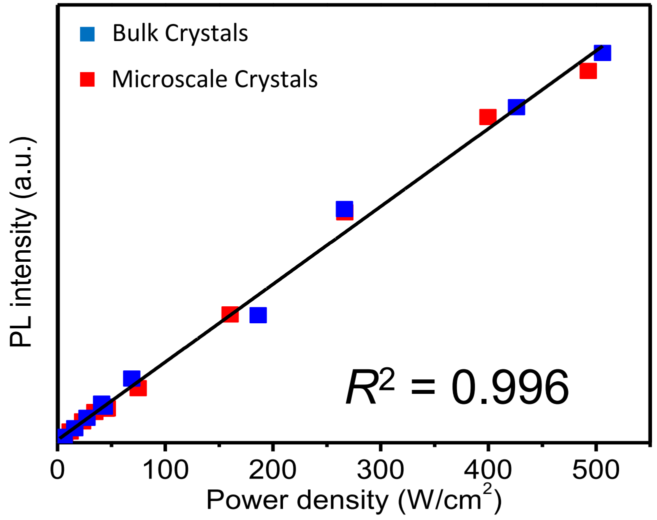


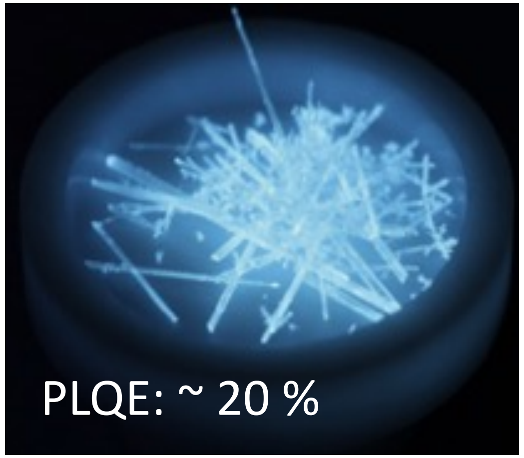


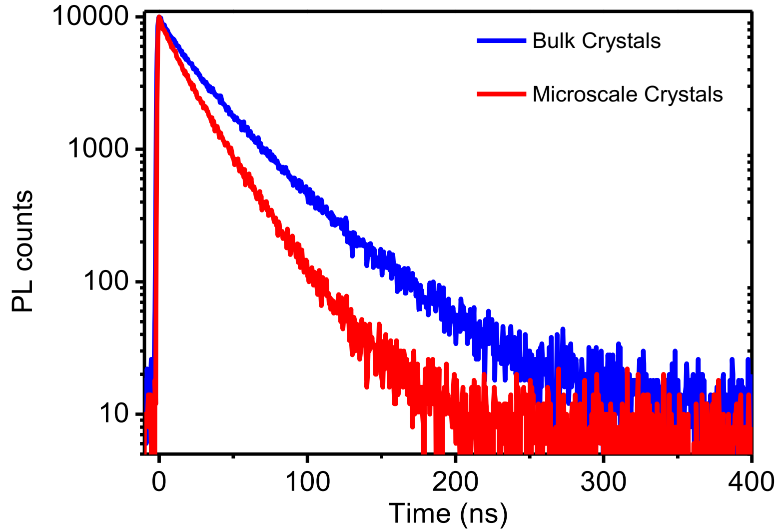
Nature Communications, **2017,** *8*, 14051

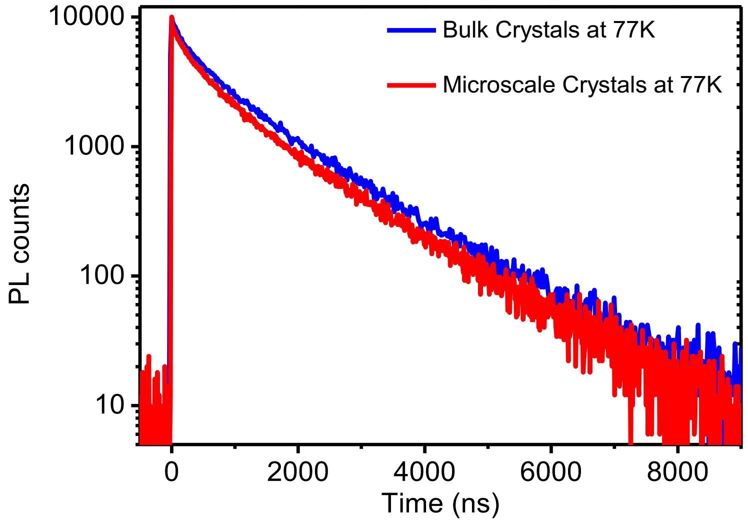
1D Organic Lead Bromide Hybrid

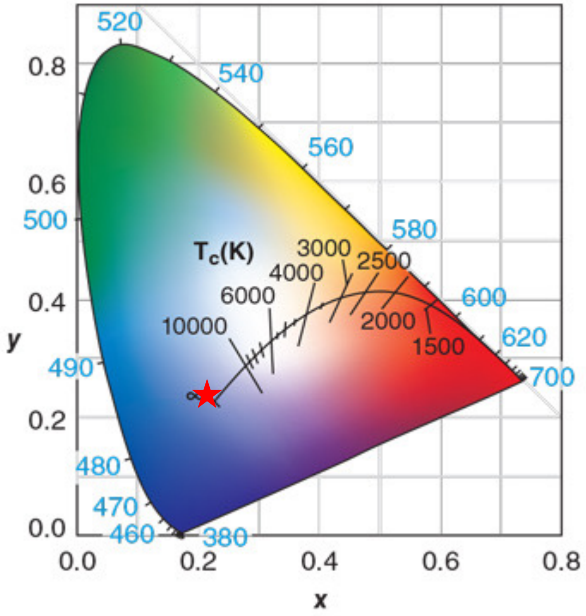










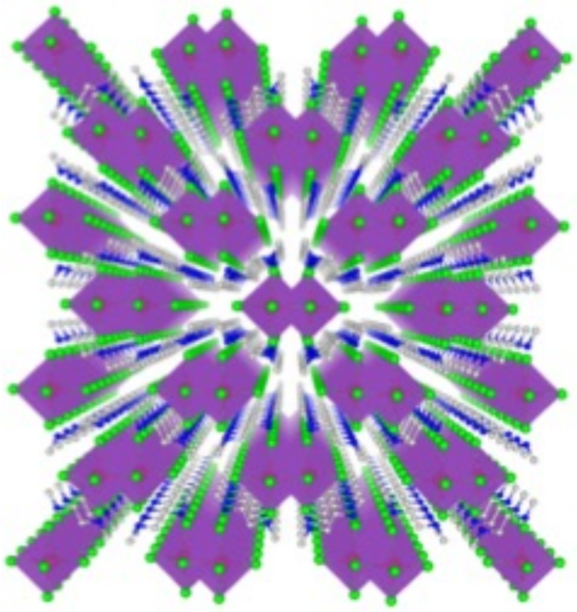


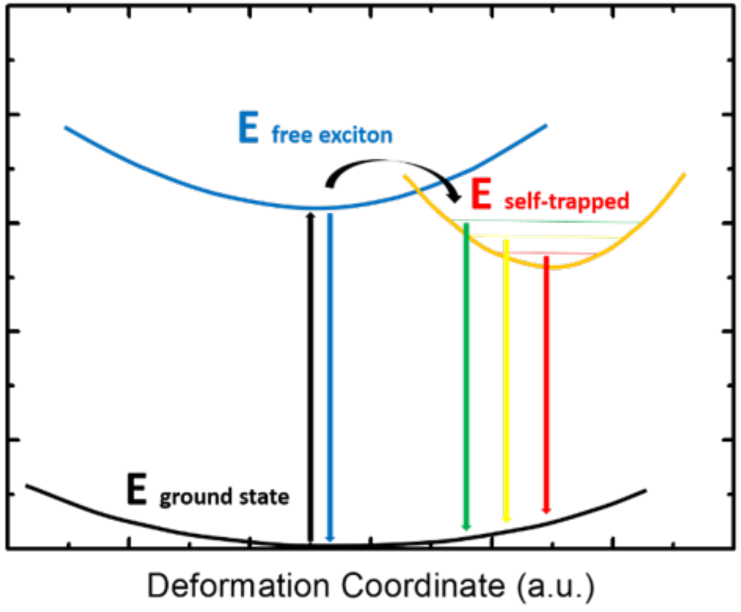
Nature Communications, **2017**, *8*, 14051

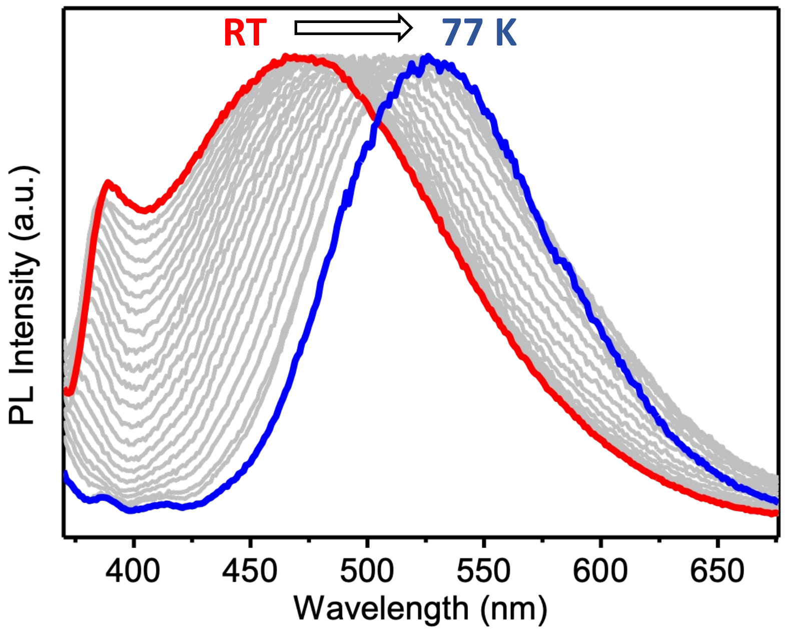
Exciton Self-Trapping

MA•GROUP
Advanced Materials for Electronics & Energy Devices

In cases of strong coupling of electrons or holes to the crystal lattice, a carrier may be self-trapped as a small polaron in its own lattice distortion field. A bound electron-hole pair involving such a carrier is generally described as a **self-trapped exciton**, and it may dramatically influence luminescence, energy transport, and lattice defect formation in the crystal. The phenomenon of exciton self-trapping is particularly common in metal halide and rare-gas crystals, where **the strong exciton-lattice coupling** can usually be ascribed to the possibility of covalent bond formation in the excited state of a crystal which does not admit such bonding in its ground state.



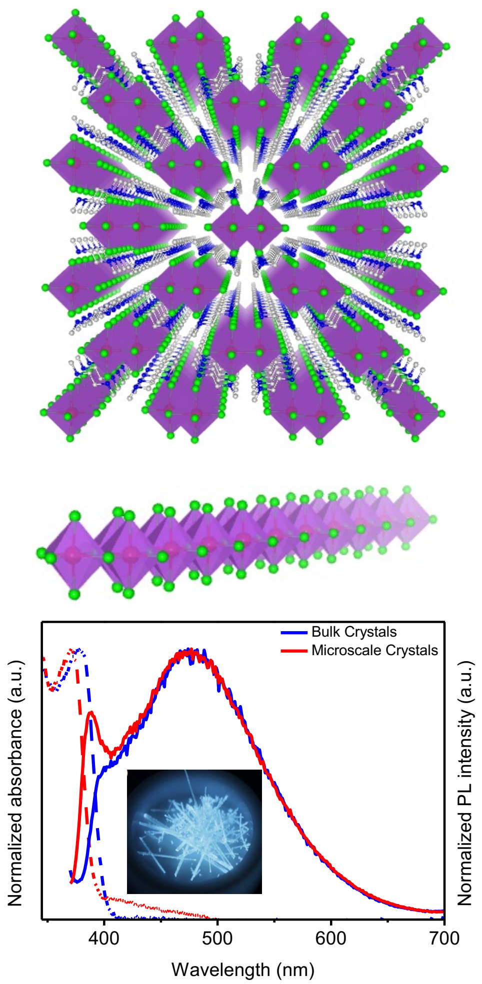




Williams, R.T. et al. *Journal of Physics and Chemistry of Solids,* **1990**, *51*, 679-716 ; Dohner, E. et al. *J. Am. Chem. Soc.,* **2014** 136, 1718-1721; Hu, T. et al. *J. Phys. Chem. Lett.,* **2016**, 7 , 2258–2263

Other 1D Structures?

1D $(C_4N_2H_{14})PbBr_4$

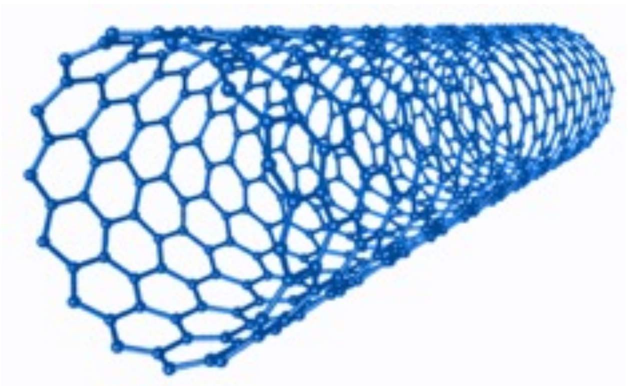


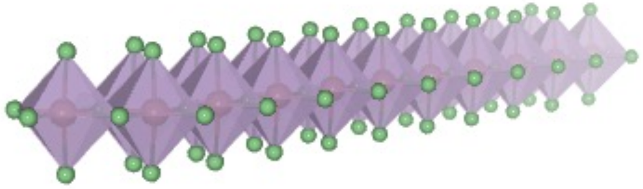
Size

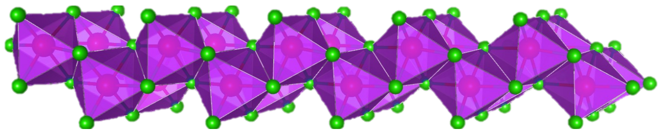
Shape

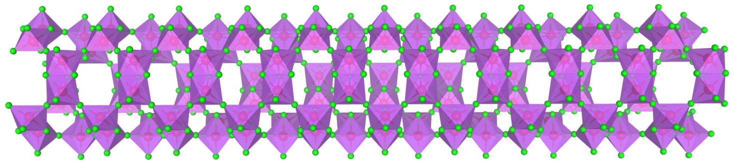
Composition

Structure



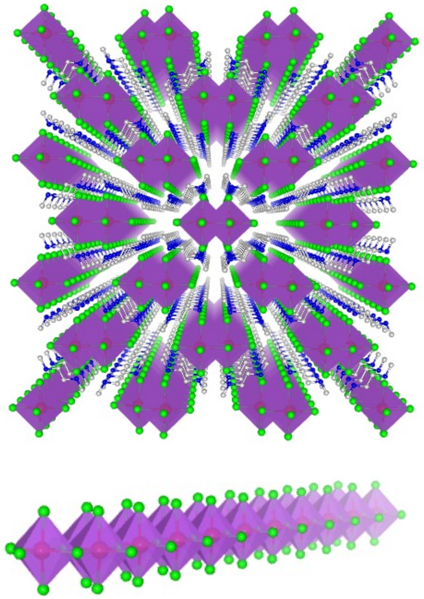


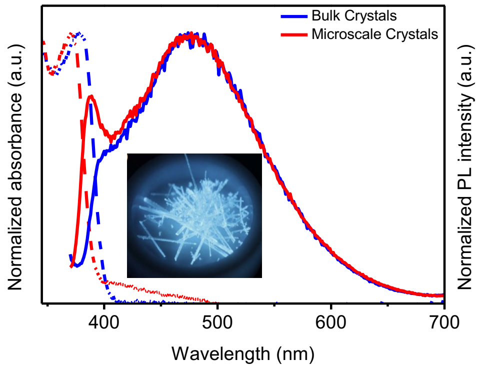




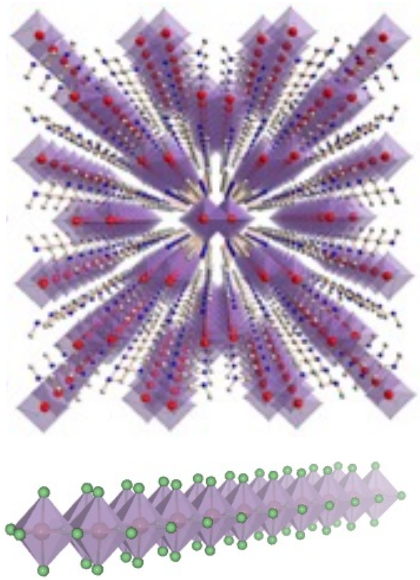
1D Organic Metal Halide Hybrids

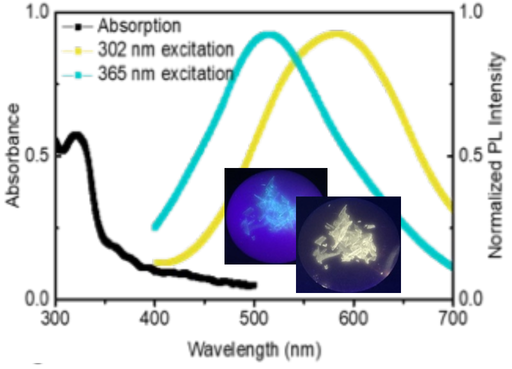
1D $(C_4N_2H_{14})PbBr_4$



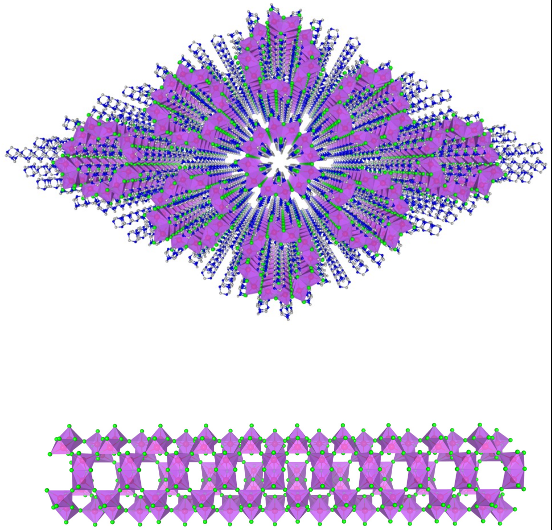


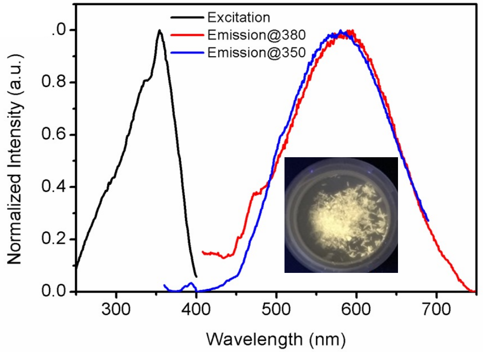
1D $(C_4N_2H_{14})PbCl_4$



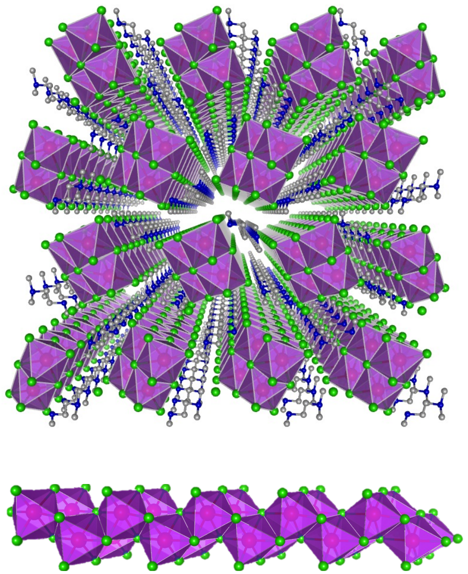


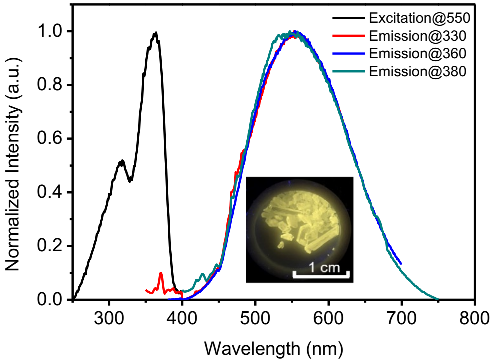
1D $(C_6N_4H_{13})_3Pb_2Br_7$





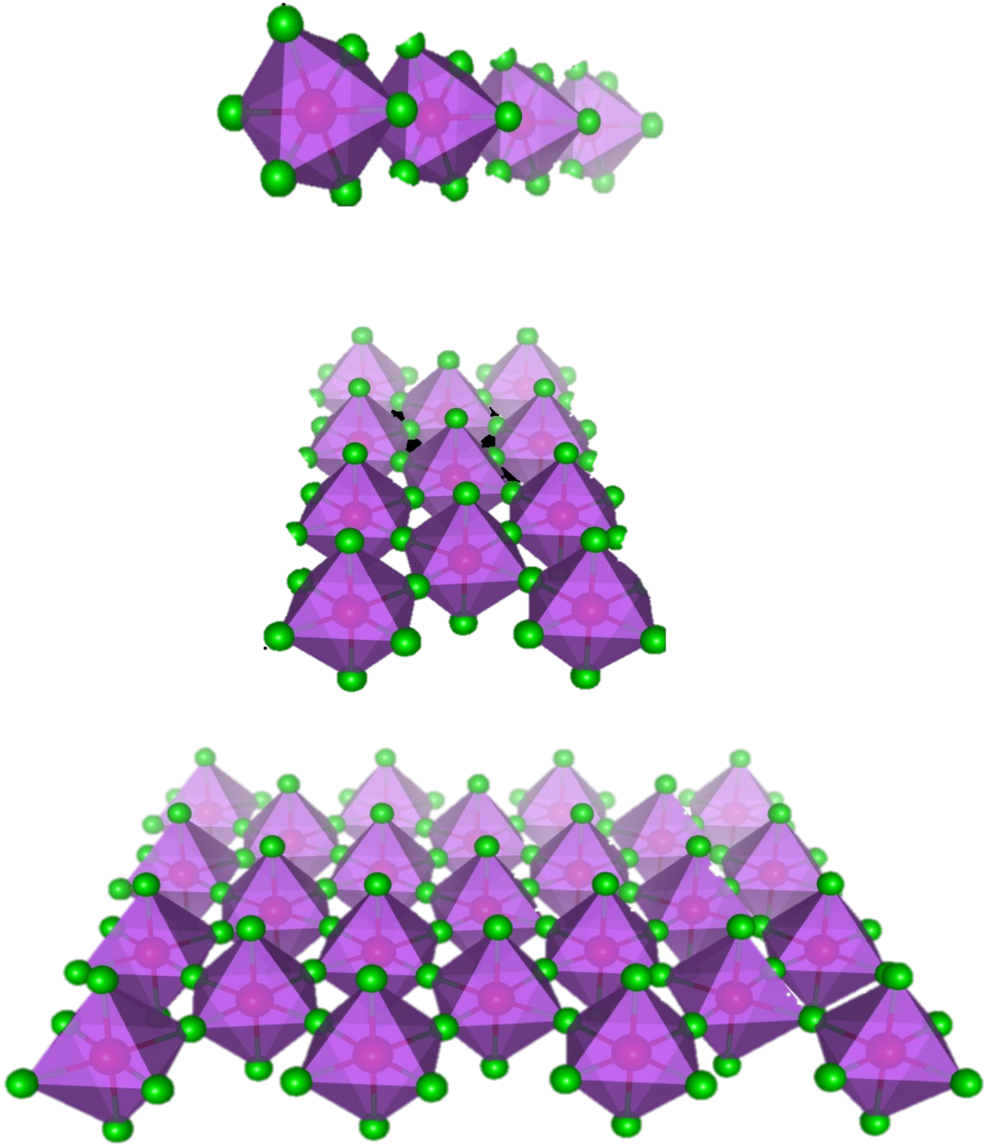
1D $(C_5N_2H_{16})Pb_2Br_6$

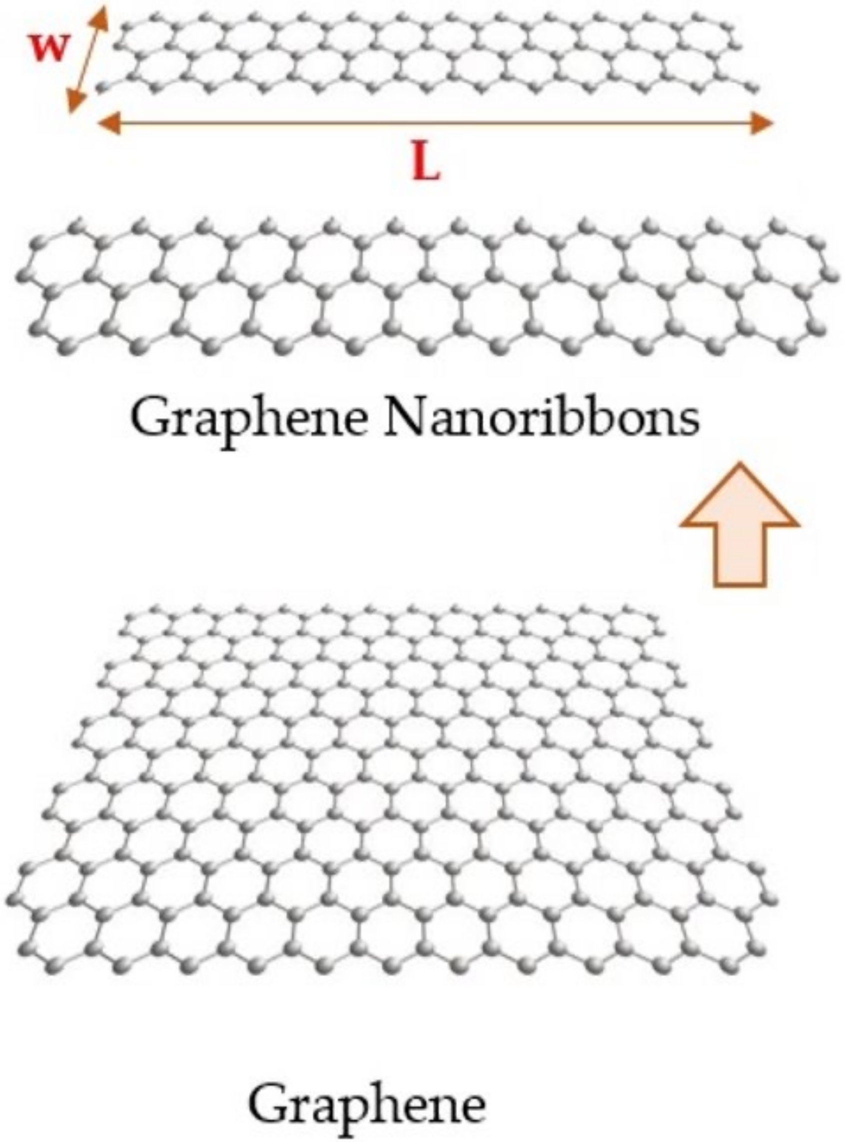




Nature Communications, **2017**, *8*, 14051; *Chemical Science*, **2017**, 8, 8400-8404; *ACS Energy Letters*, **2018**, *3*, 1443-1449; *Advanced Optical Materials*, **2019**, *7*, 1801474

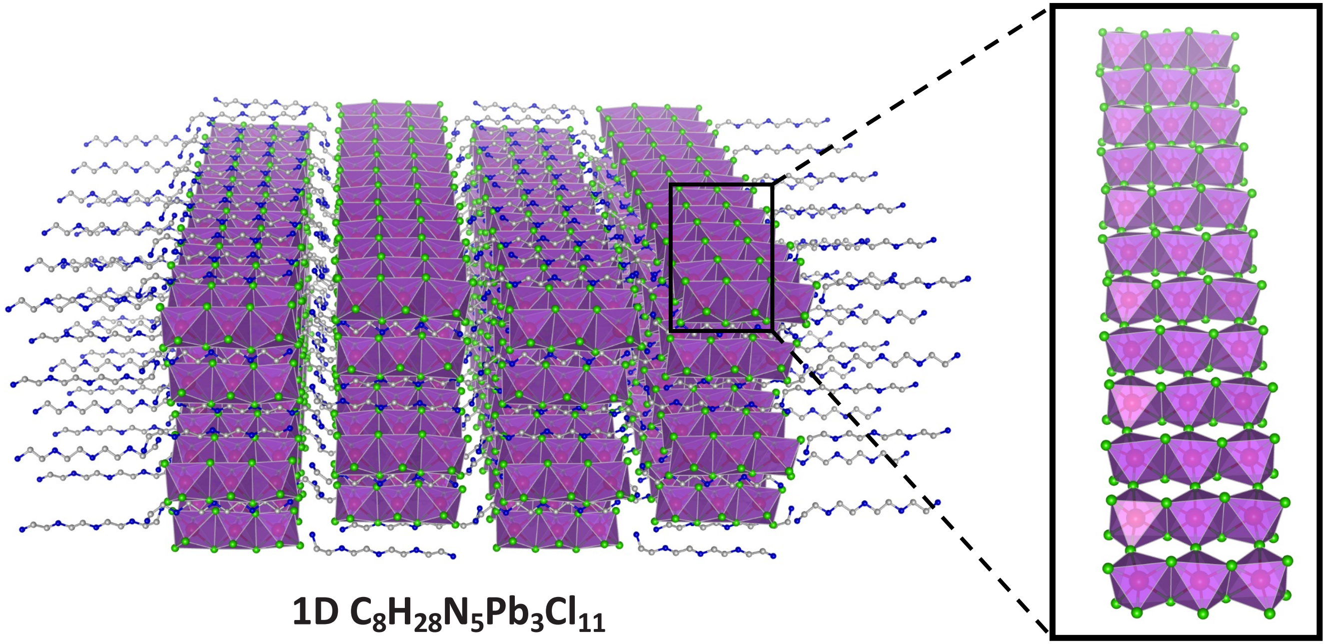
Metal Halide Nanoribbons



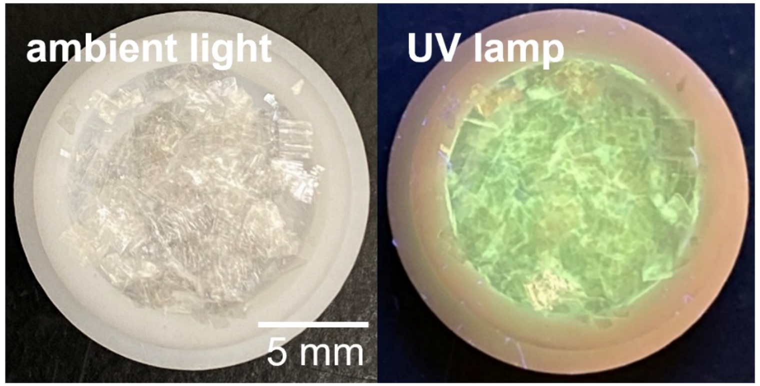


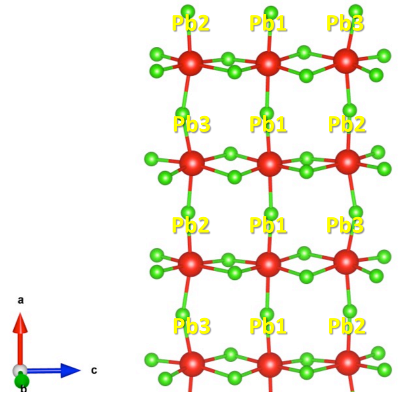
MA·GROUP
Advanced Materials for Electronics & Energy Devices

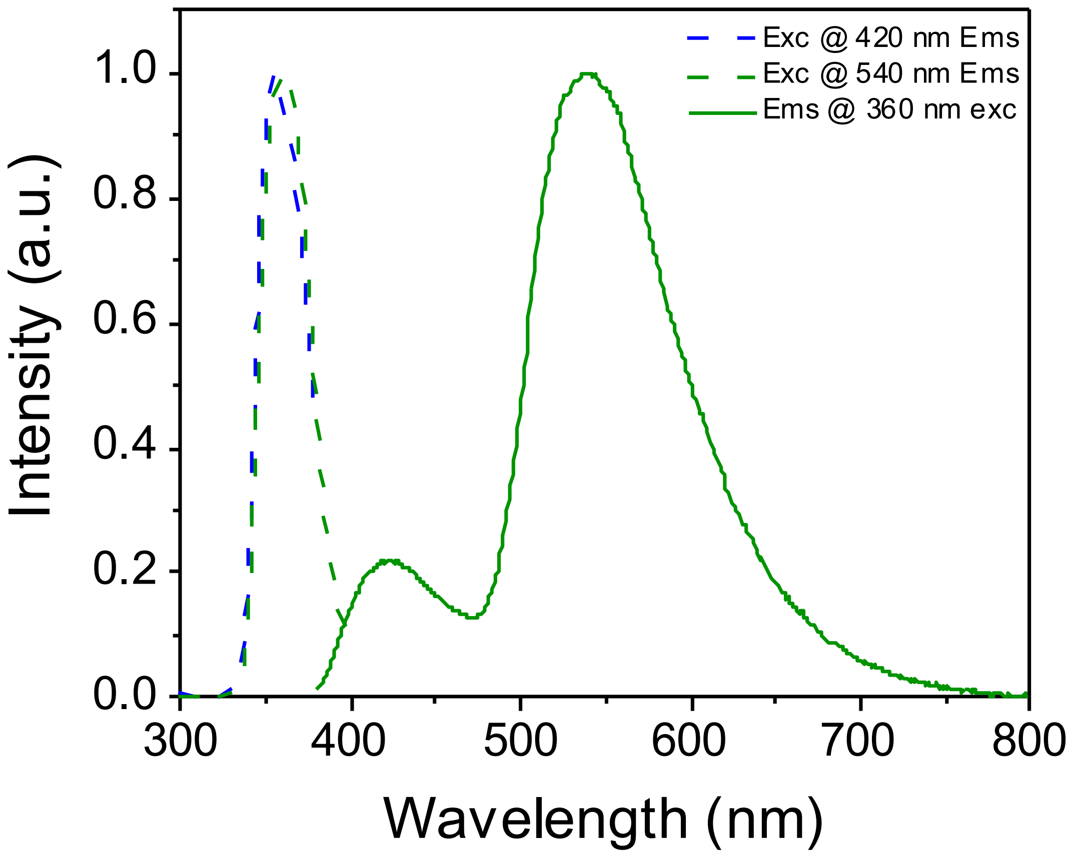
1D Organic Metal Halide Nanoribbons



1D $C_8H_{28}N_5Pb_3Cl_{11}$

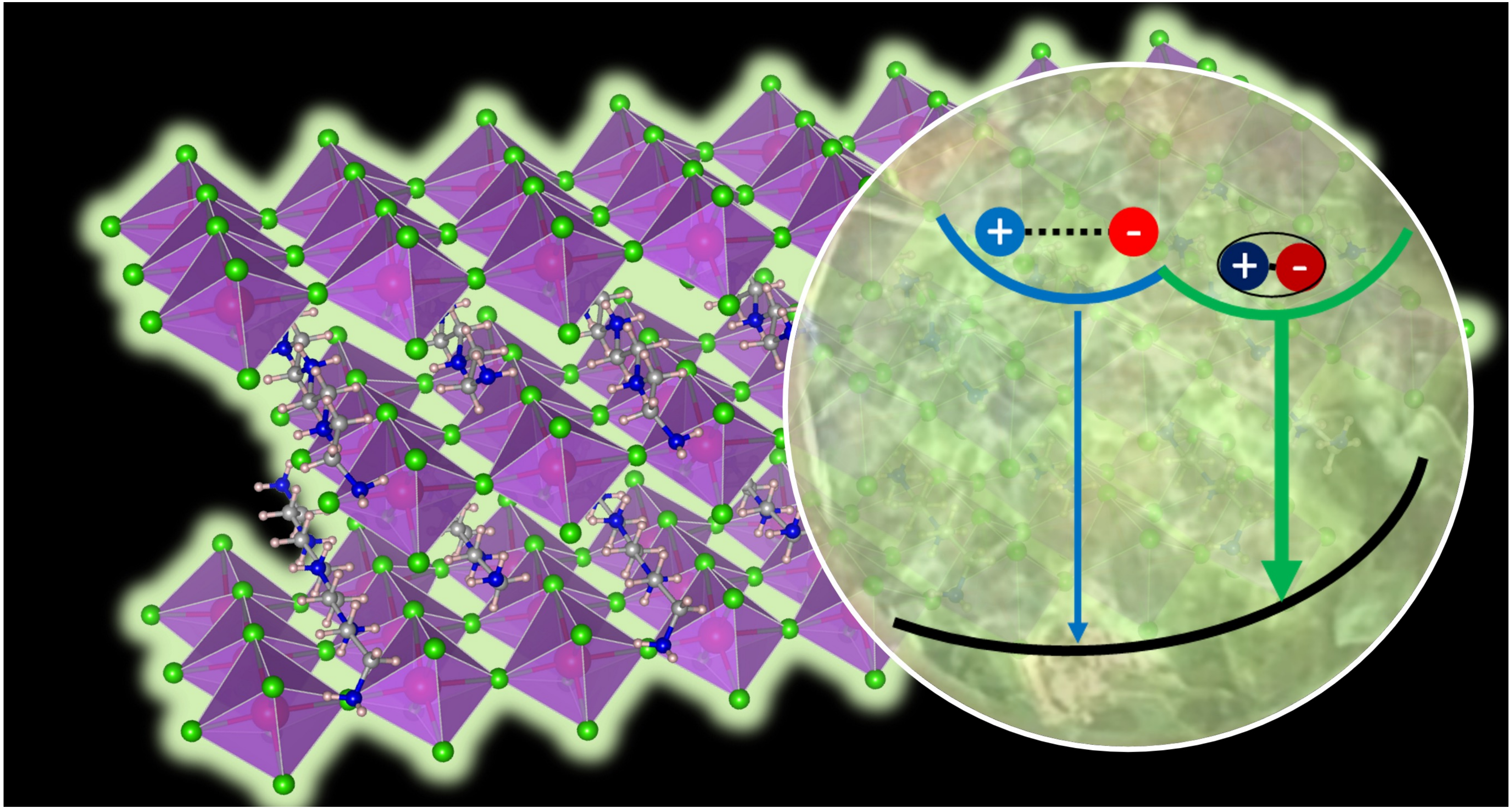






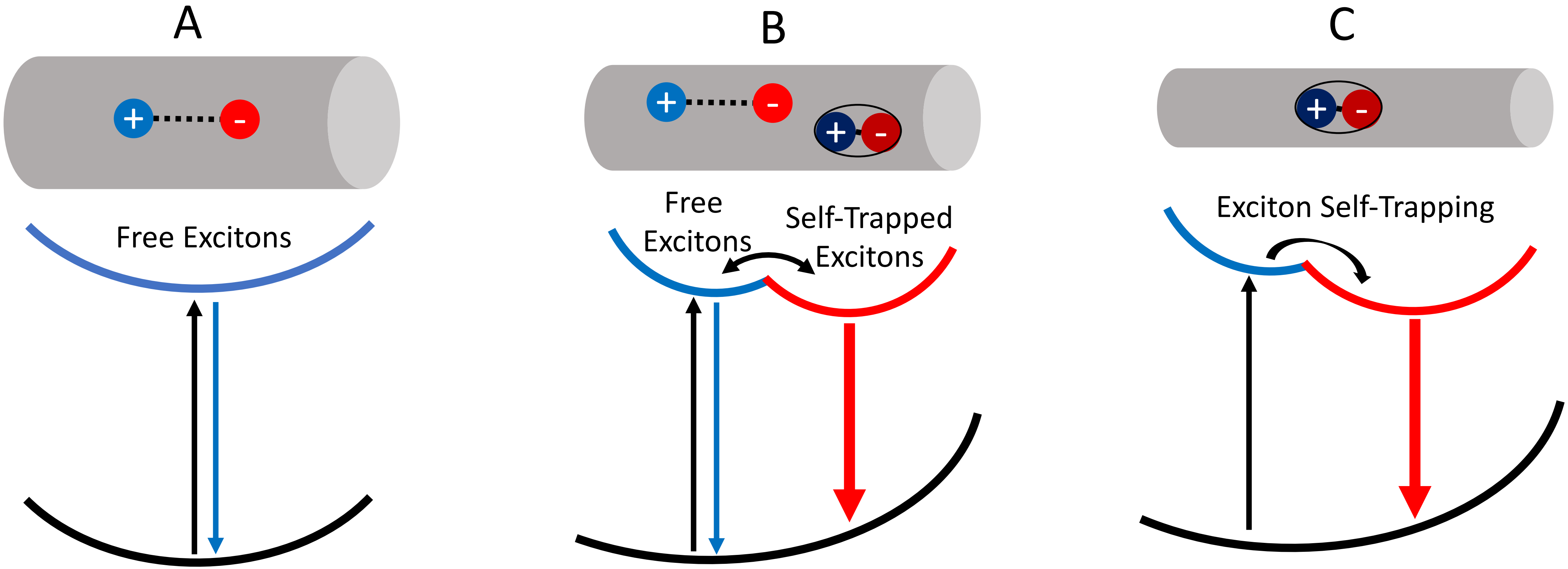
Chemical Communications, **2023**, *59*, 3711-3714

1D Organic Metal Halide Nanoribbons



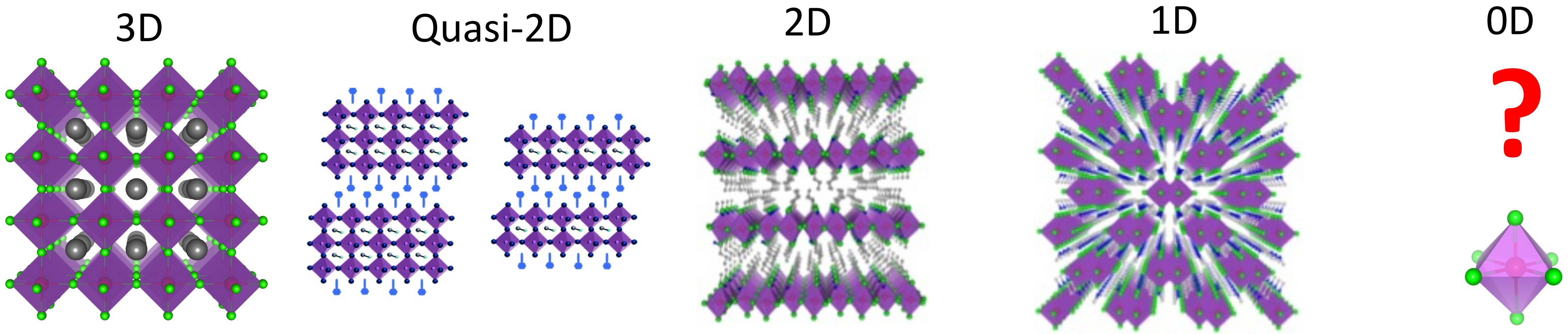
Chemical Communications, **2023**, *59*, 3711-3714

Free and Self-Tapped Excitons

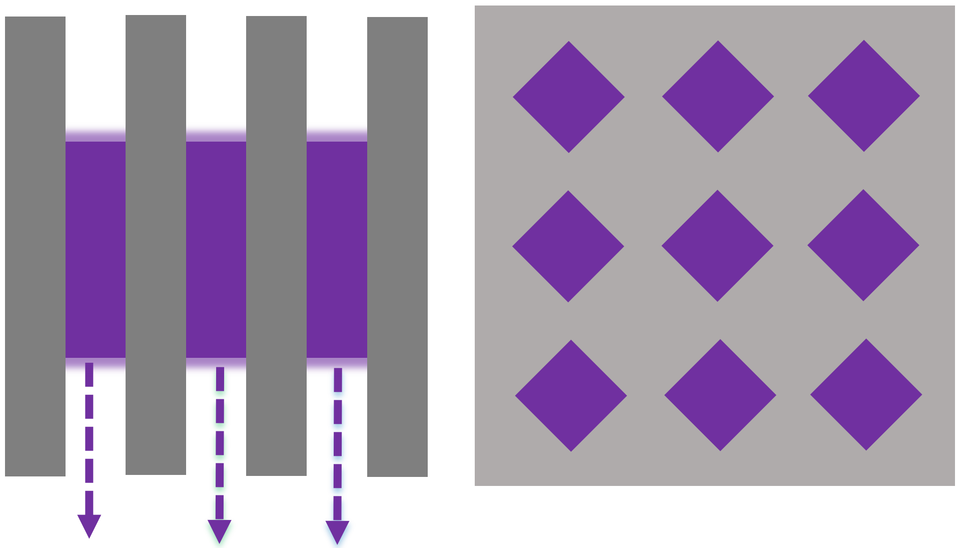


(A) Direct band formation with free excitons only resulting in narrow emission. (B) Thermally activated equilibrium between direct band free exciton excited state and self-trapped excited state resulting in emissions from both excited states: narrow high energy emission from free excitons and below-gap broadband emission from self-trapped excitons. (C) Spontaneous exciton self-trapping to form localized excitons with below-gap broadband emission.

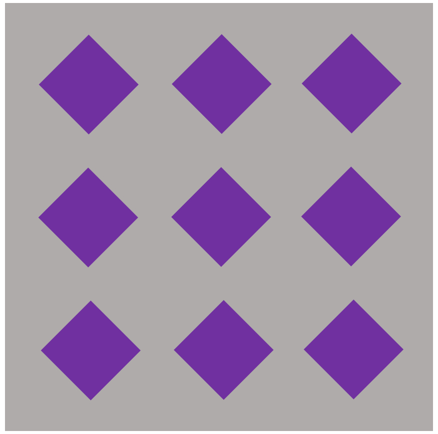
From 3D to 2D, 1D, and 0D?

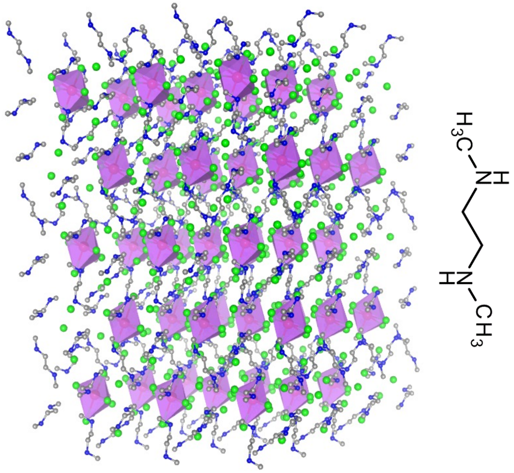


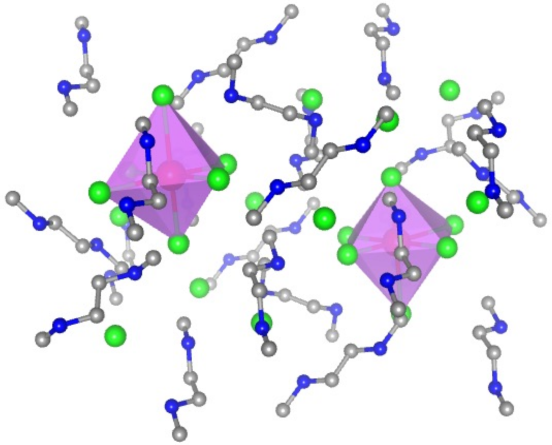
The isolation of the photoactive metal halide species by the wide band gap organic ligands leads to no interaction or electronic band formation between the metal halide species, allowing the bulk materials to exhibit the intrinsic properties of individual metal halide species. 0D organic metal halide hybrids can be considered as perfect host-guest systems, with metal halide species periodically doped in the organic matrix.

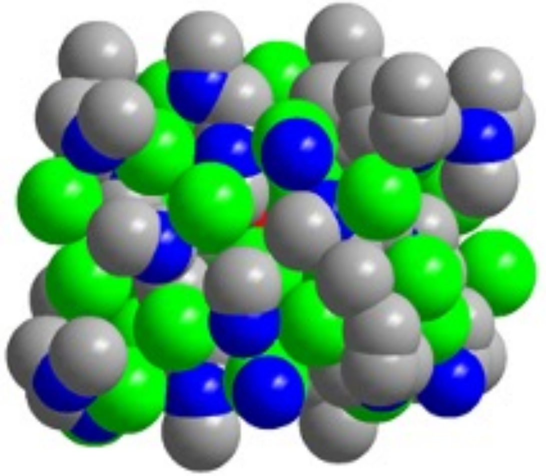


0D Organic Metal Halide Hybrids

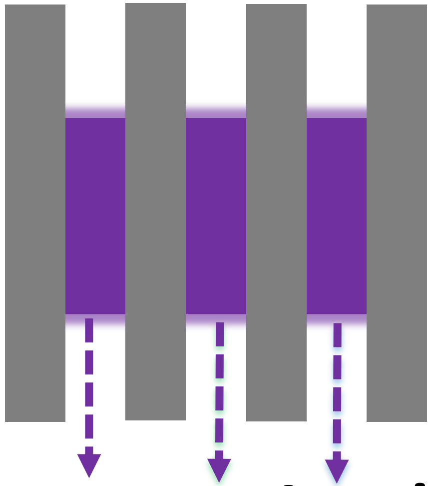


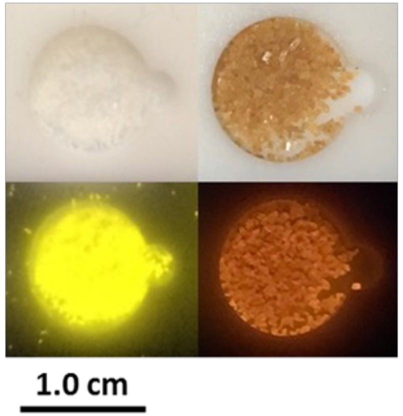


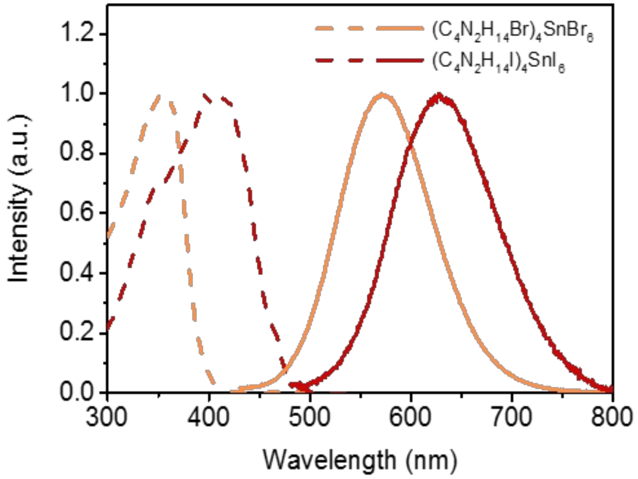


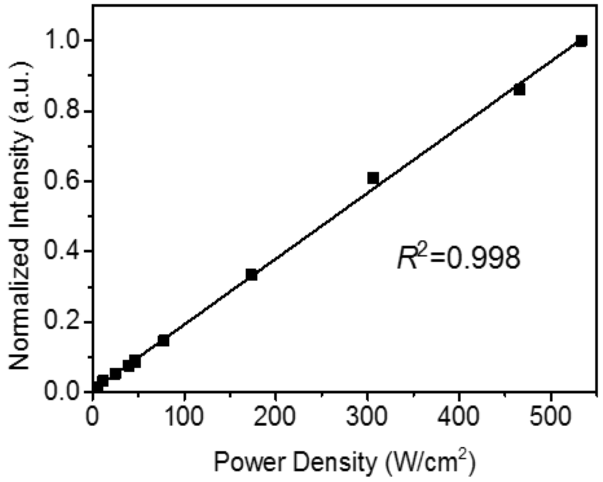


Perfect Host-Guest System





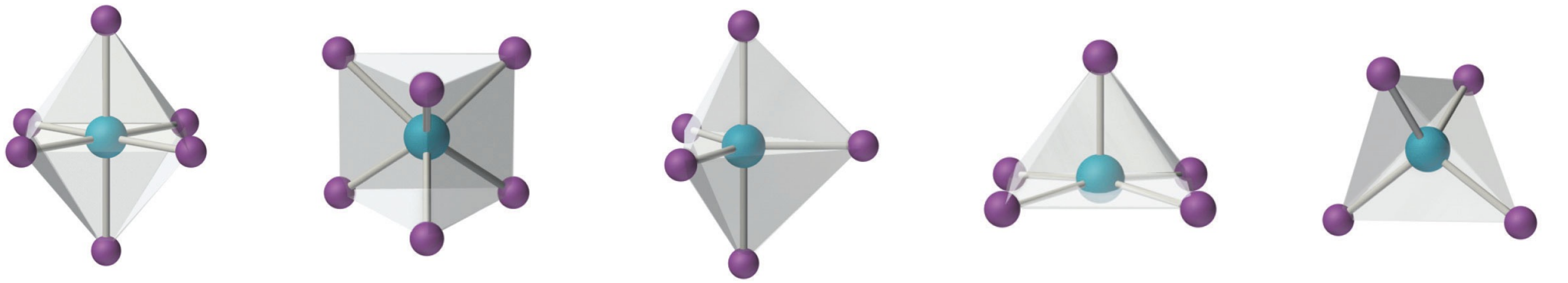




Luminescent 0D Sn halide hybrids with near-unity PLQE!

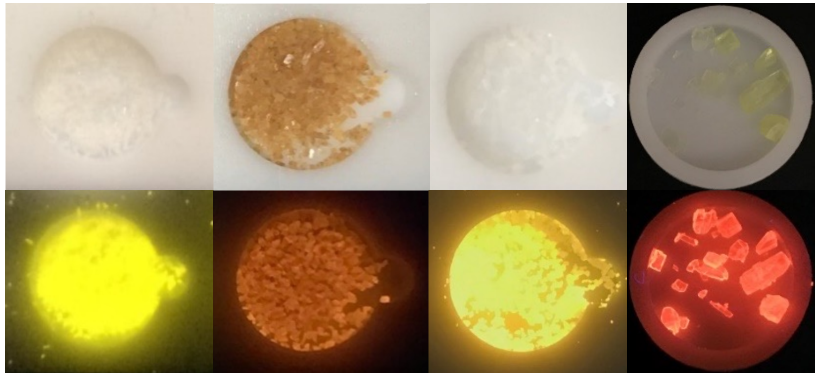
Angewandte Chemie International Edition, **2017**, 56, 9018-9022; *Chemical Science*, **2018**, *9*, 586-593.

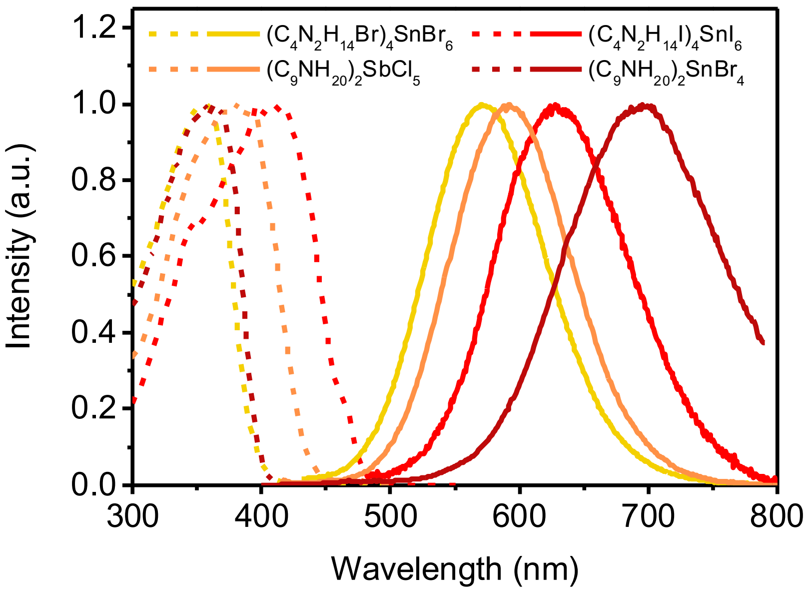
A General Concept

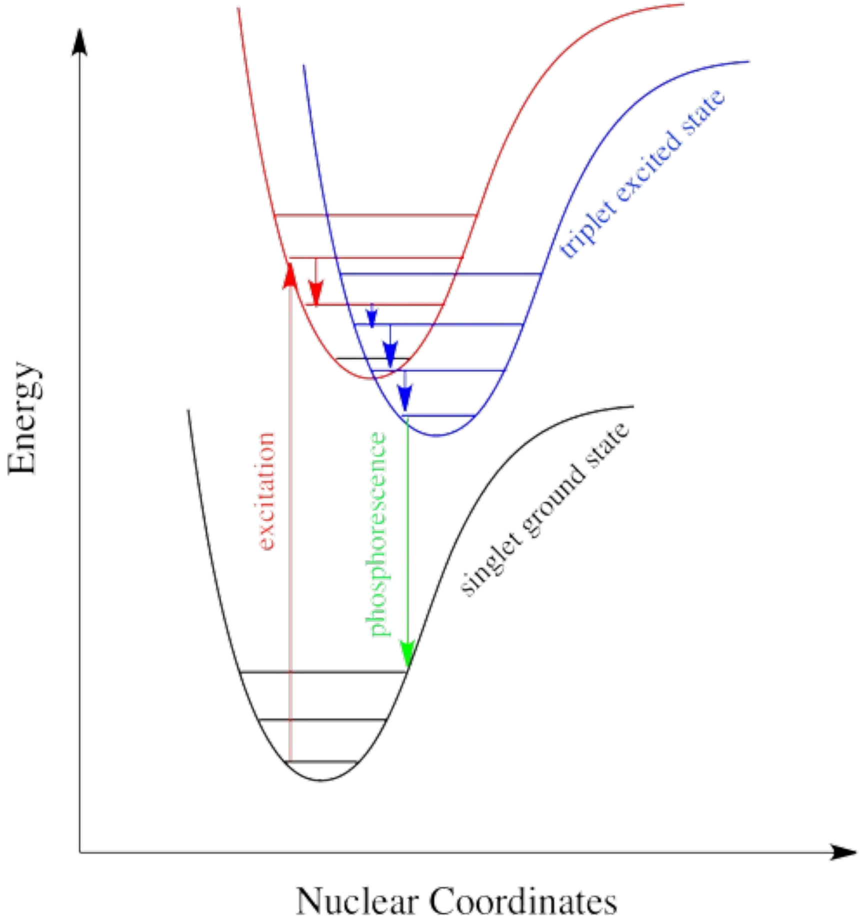


Octahedral MX_6	Trigonal Prismatic MX_6	Trigonal Bipyramidal MX_5	Square Pyramidal MX_5	Tetrahedral MX_4

0D $SnBr_6$ 0D SnI_6 0D $SbCl_5$ 0D $SnBr_4$

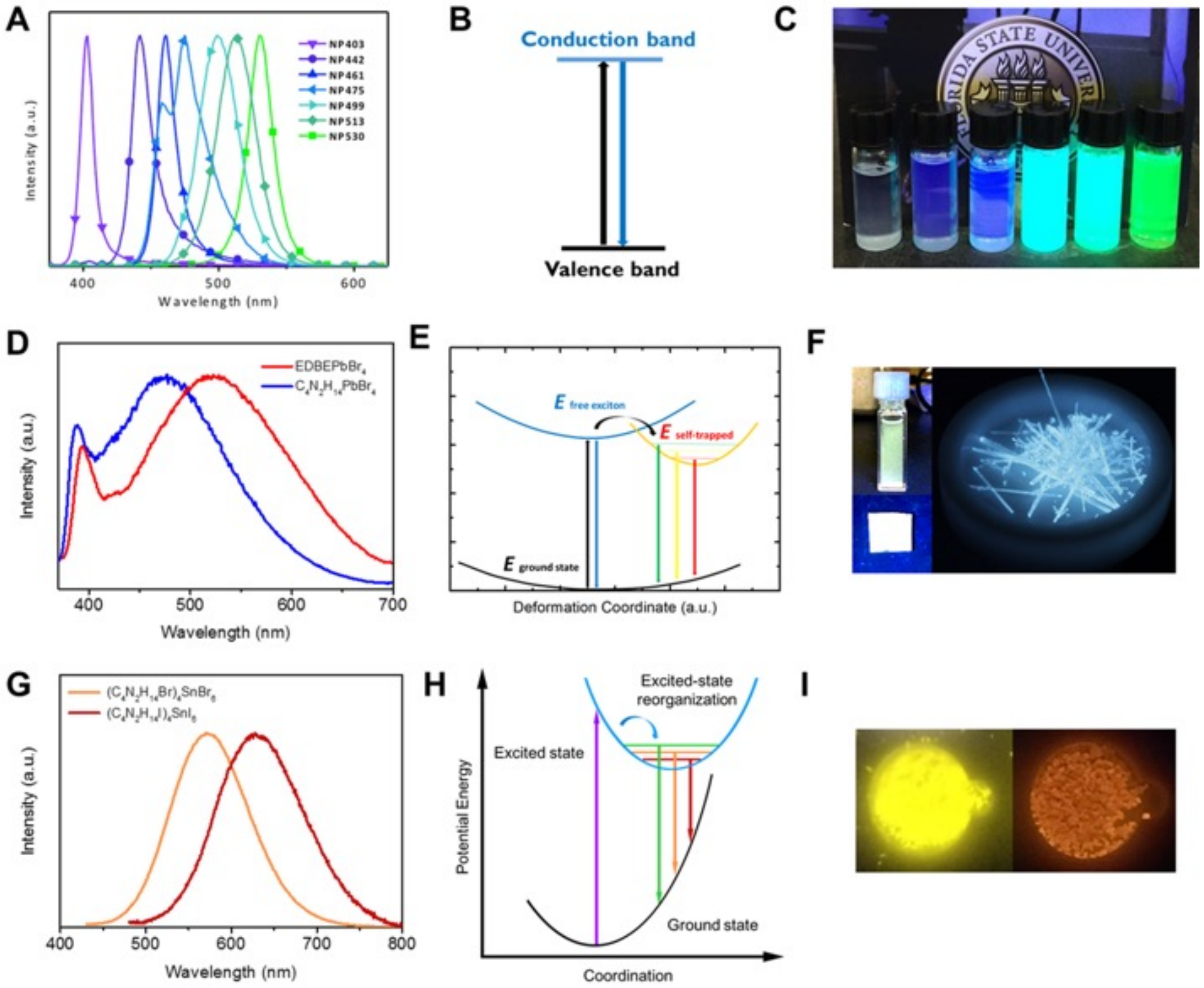






Chemical Science, **2018**, *9*, 586-593; *Chemistry of Materials*, **2018**, *30*, 2374-2378; *Angewandte Chemie International Edition*, **2017**, *56*, 9018-9022; **2018**, *57*, 1021-1024

Dimensionality Dependence



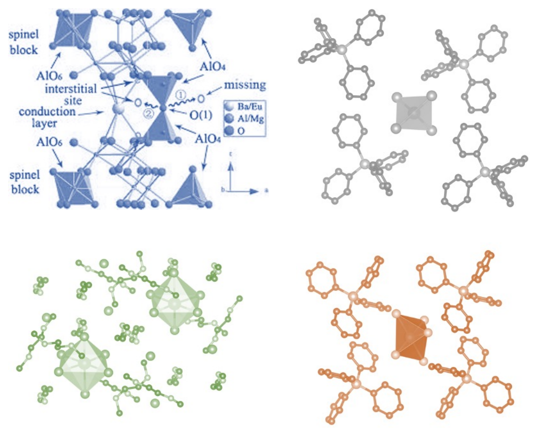
3D and 2D: With band formation and little structure distortion, have emissions from the direct excited states, narrow, small stokes shift, and short lifetimes.

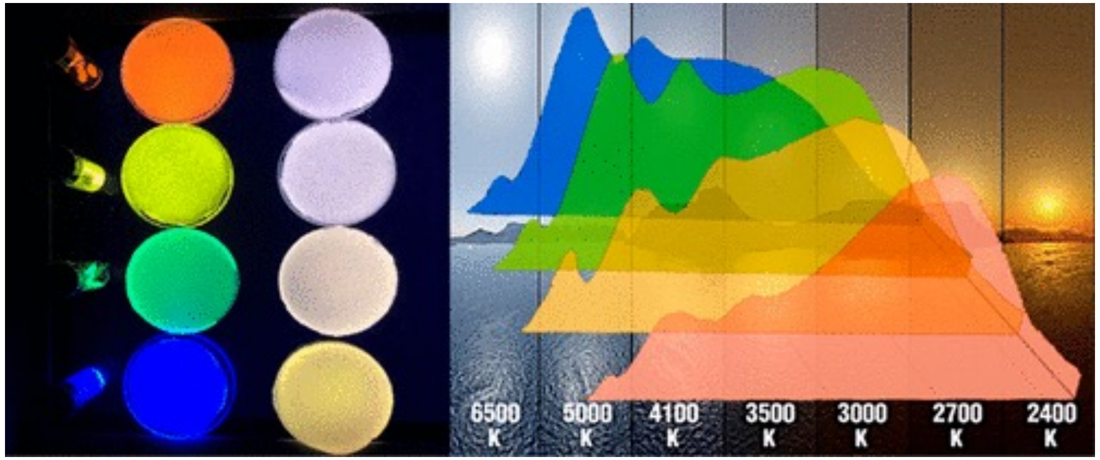
Corrugated-2D and 1D: With band formation and structure distortion, have broadband emissions from both direct and self-trapped excited states.

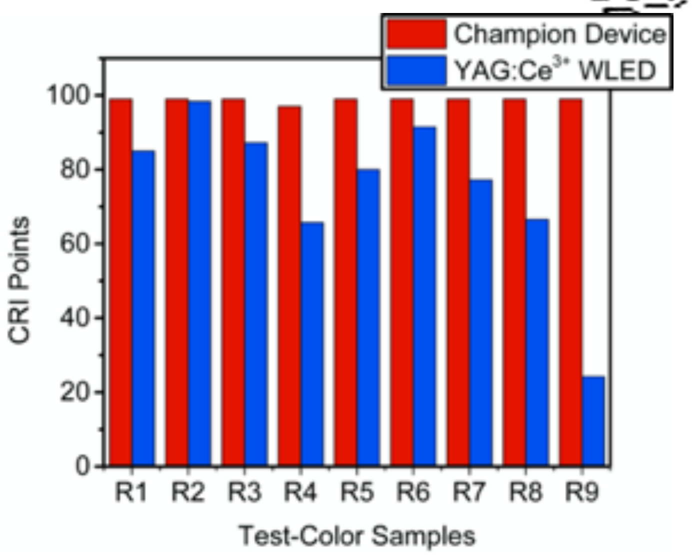
0D: No interactions between metal halide octahedrons or band formation, have emissions from the distorted excited states only, broadband, large stokes shift, and long lifetimes.

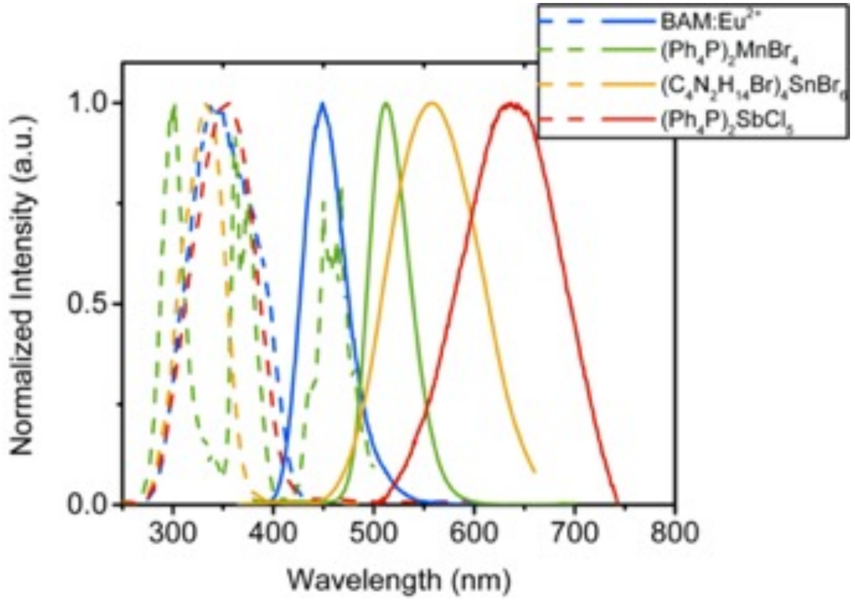
ACS Energy Letters, **2018**, *3*, 54-62; *Materials Research Letters*, **2018**, *6*, 552-569; *Materials Science & Engineering - R: Reports*, **2019**, *137*, 38-65; *Advanced Optical Materials*, **2021**, *9*, 2001766

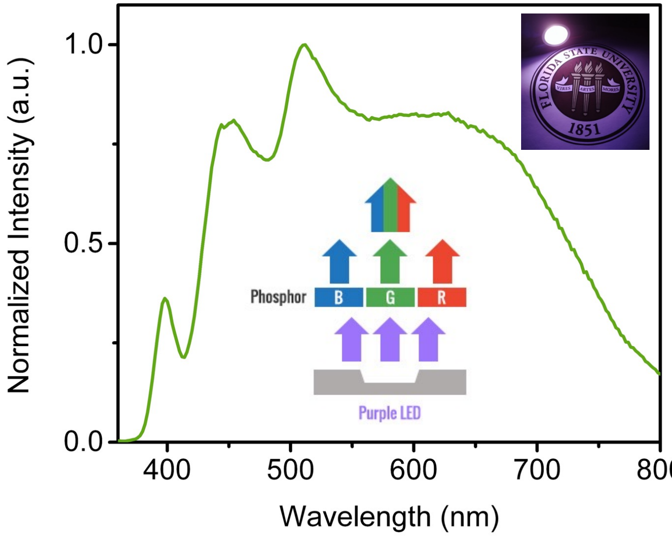
Application I: UV Pumped White LEDs

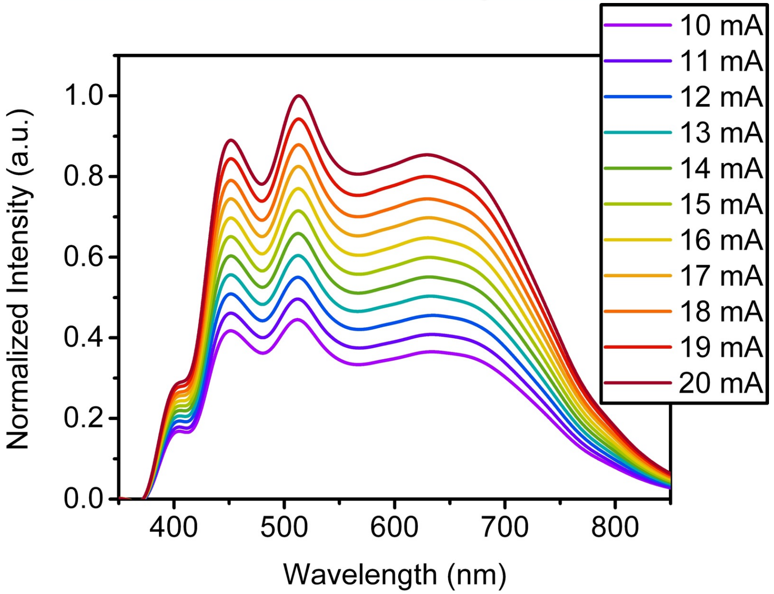






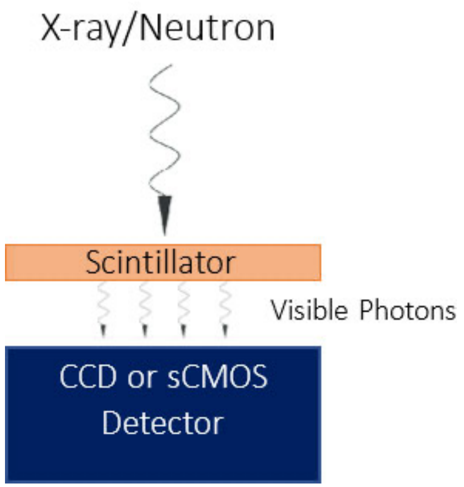


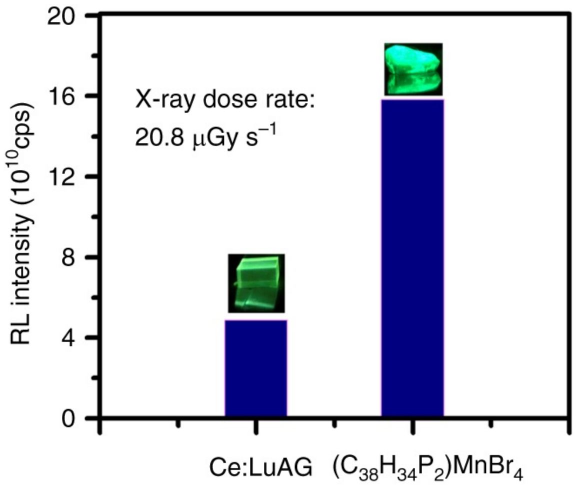


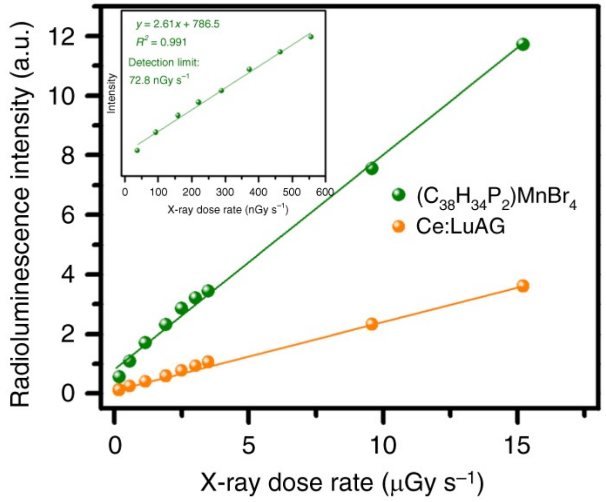


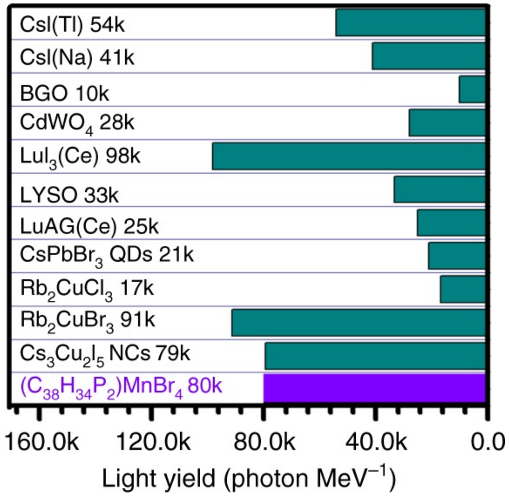
Chemical Science, **2018,** *9*, 586-593; *ACS Applied Materials and Interfaces*, **2018**, *10*, 30051-30057; *APL Materials*, **2020**, *8*, 010902

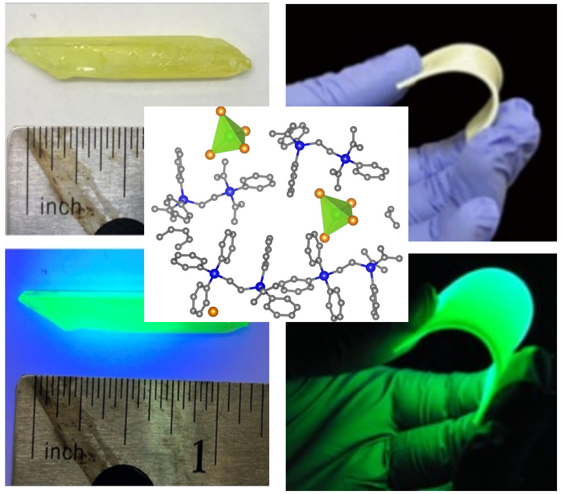
Application II: X-Ray Scintillators

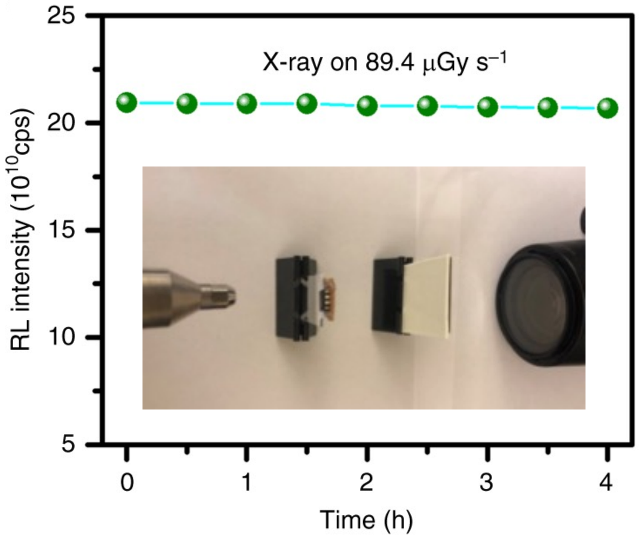


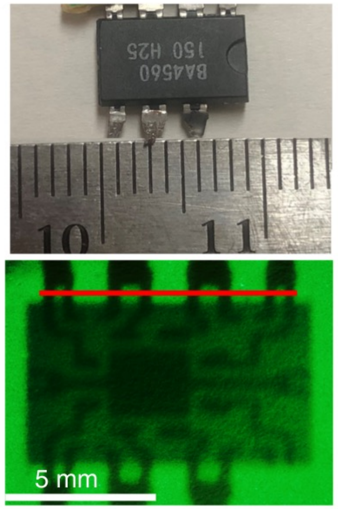


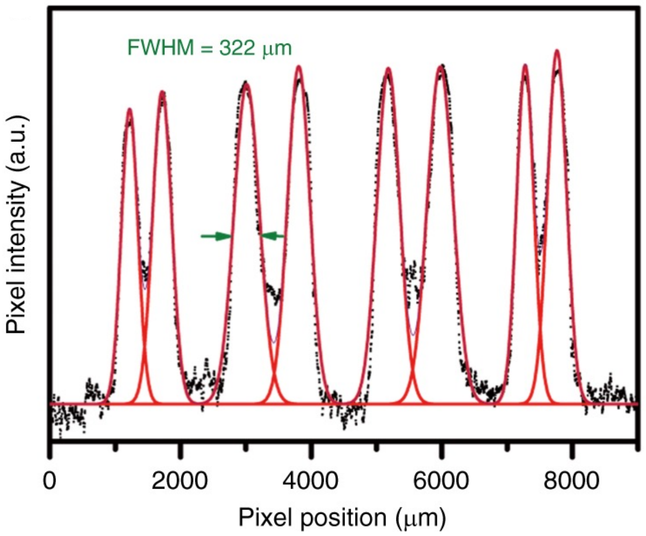






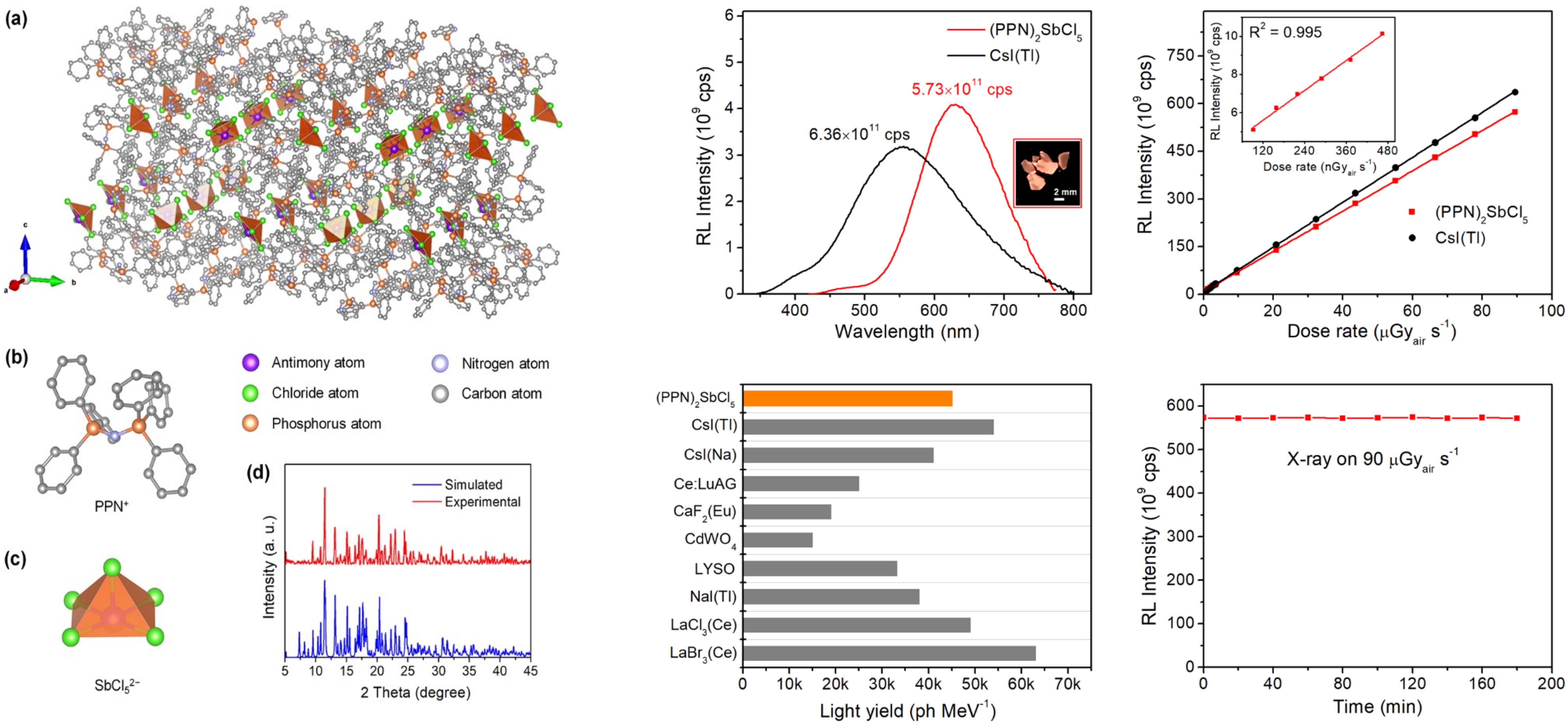






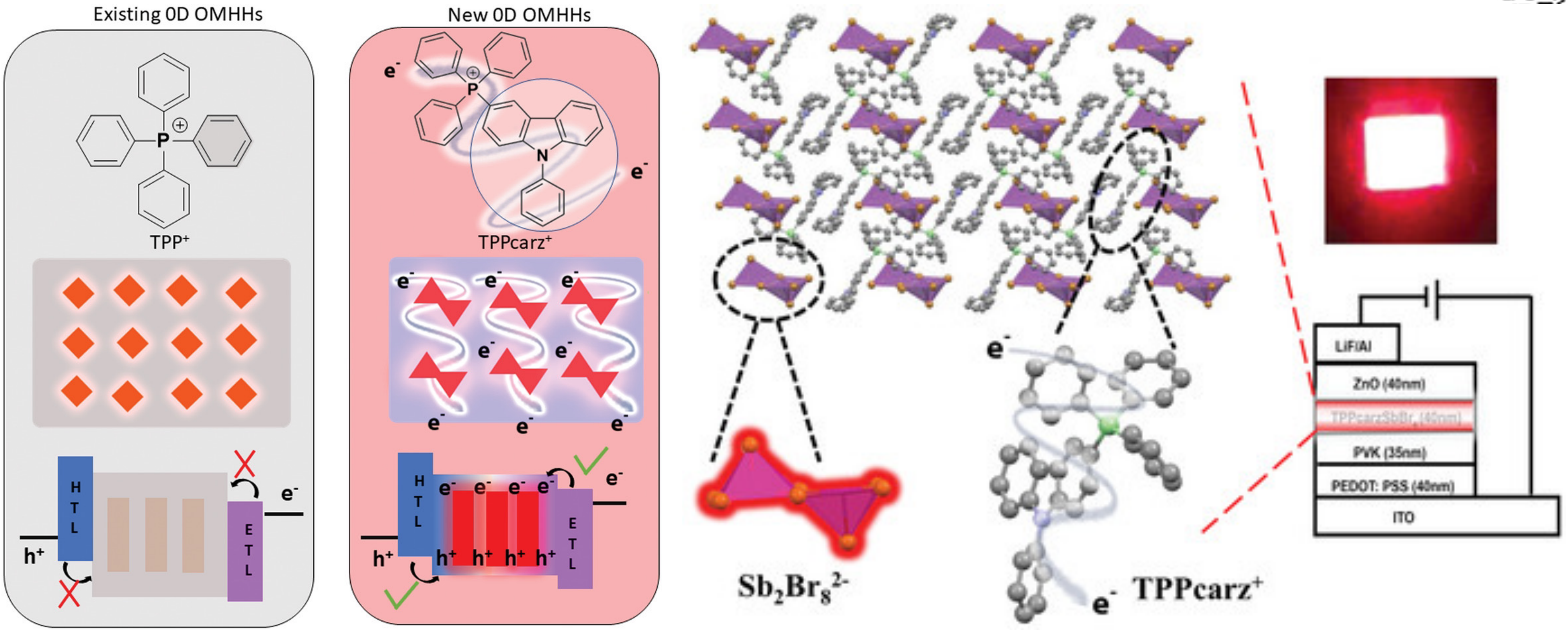
Nature Communications, **2020**, *11*, 4329

Application II: X-Ray Scintillators



ACS Materials Letters, **2020**, *2*, 633–638

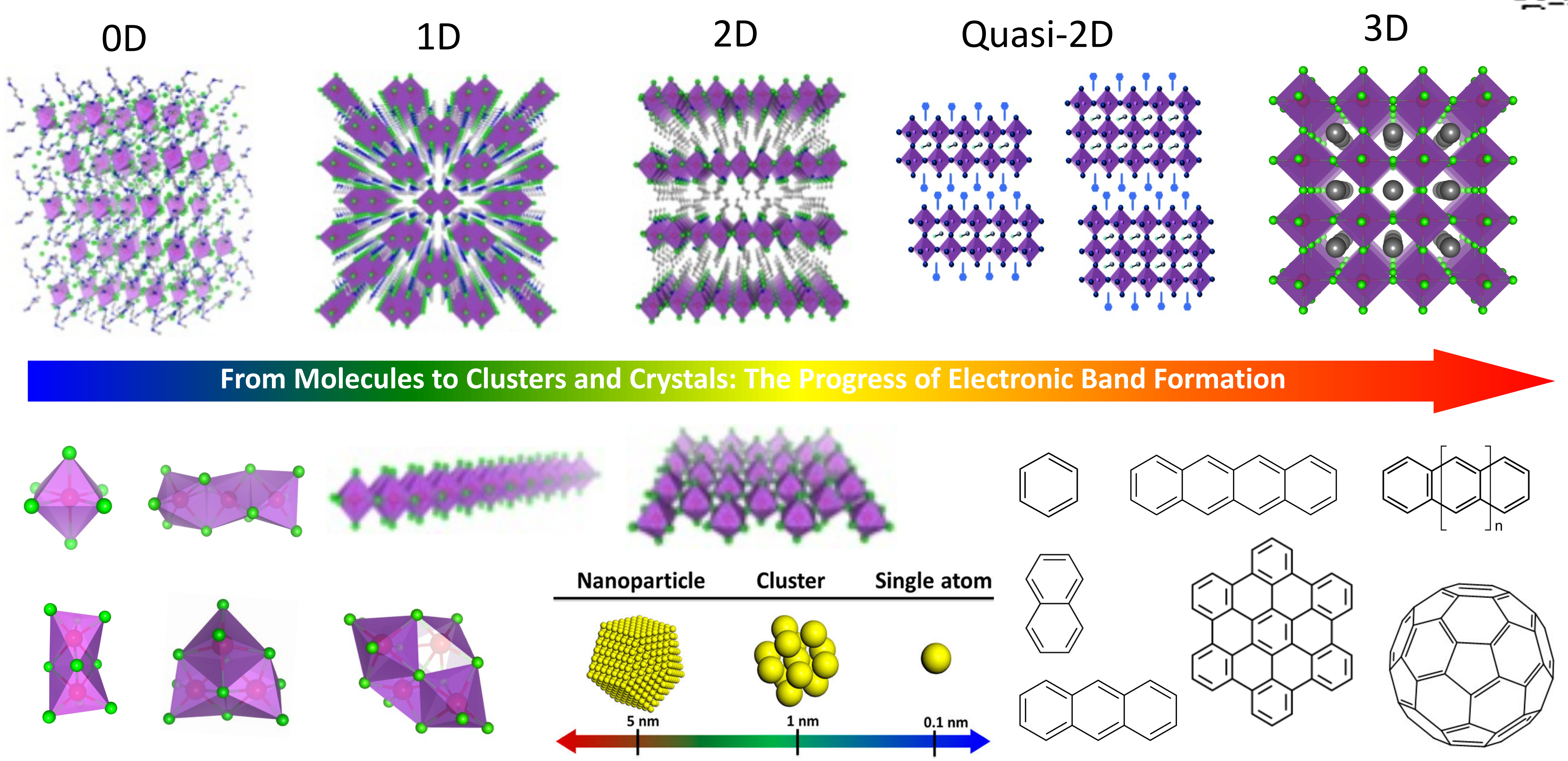
Application III: Electrically Driven LEDs



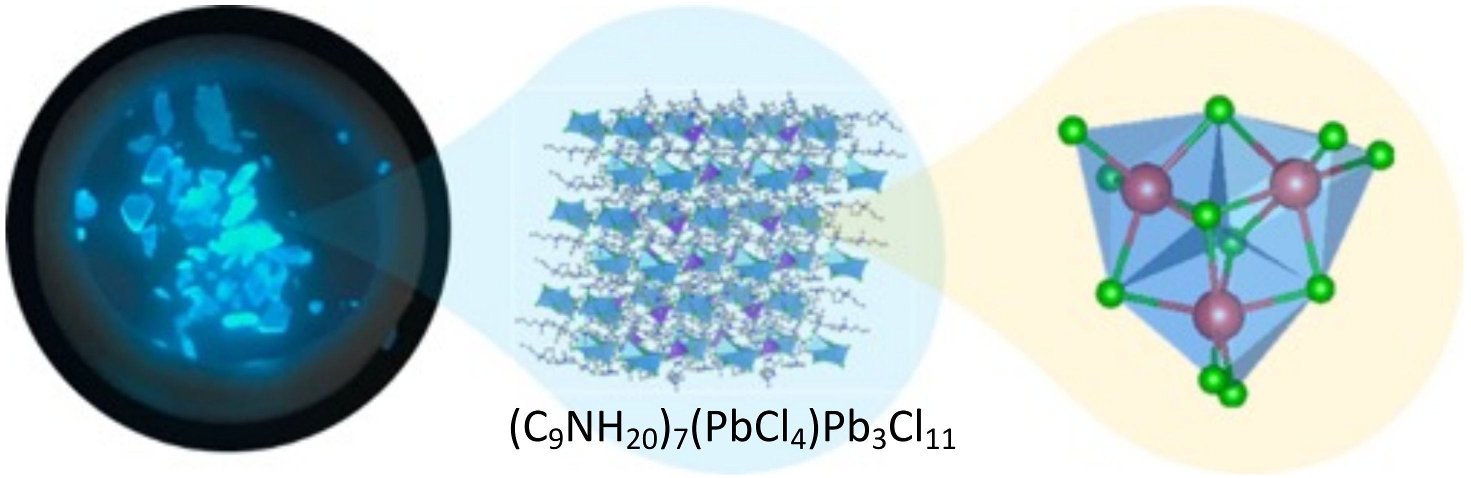
A highly luminescent 0D organic antimony bromide hybrid containing semiconducting organic cation is developed for the first time, with which electrically driven LEDs are fabricated to exhibit an EQE of 5.12%, a peak luminance of 5957 cd m^{-2}, and a current efficiency of 14.2 cd A^{-1}.

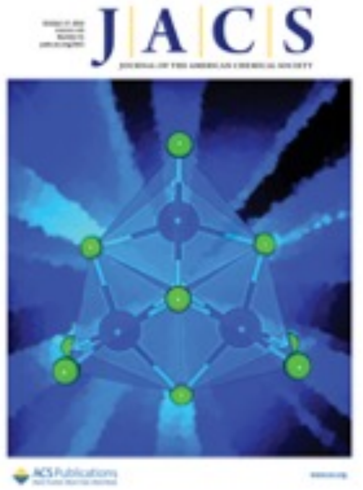
Advanced Materials, **2023**, *35*, 2209417

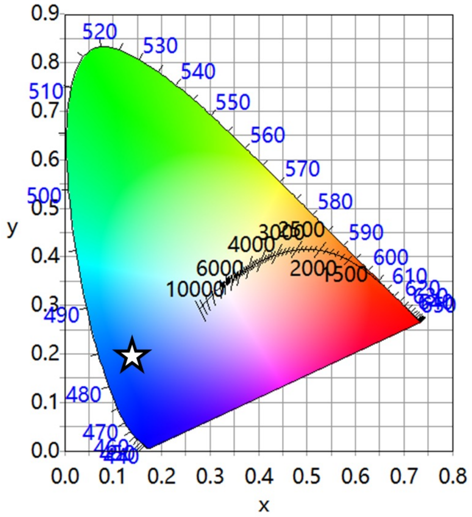
Molecules, Clusters, Crystals

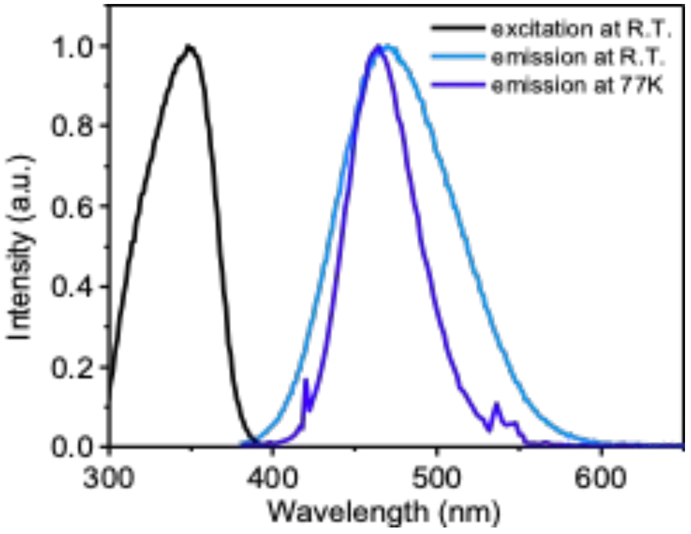


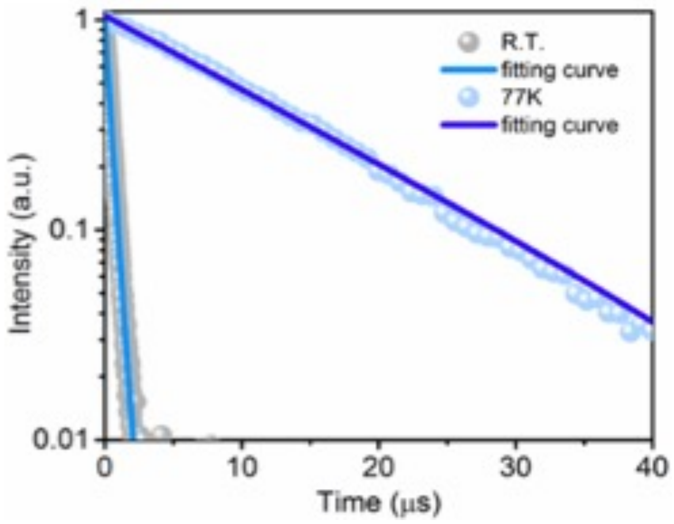
Metal Halide Clusters

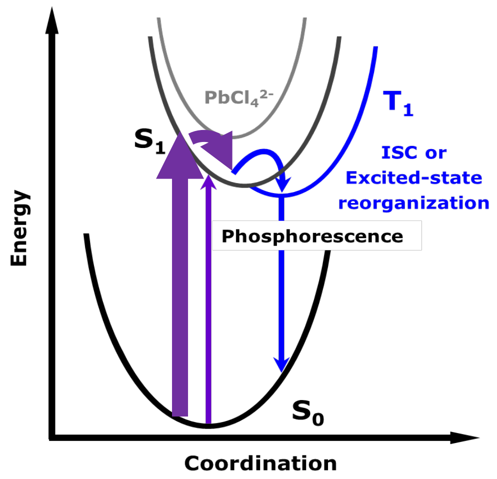






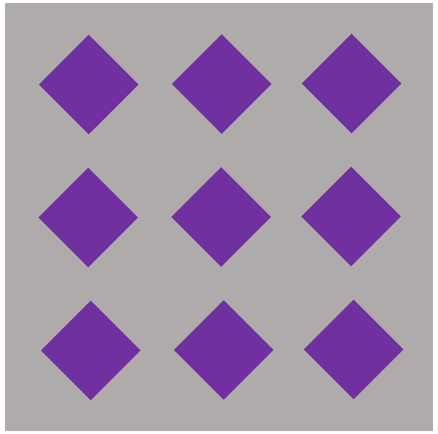




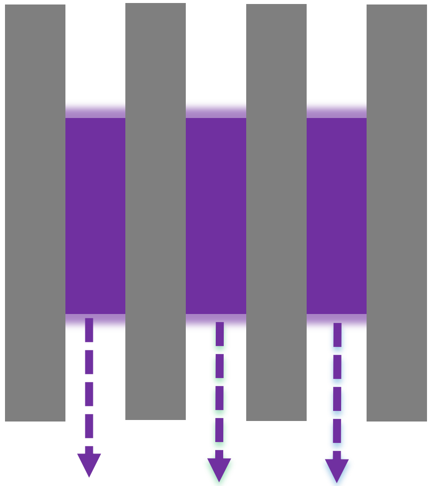


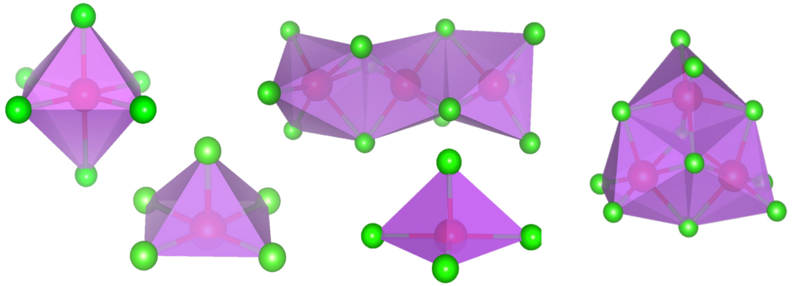
Journal of The American Chemical Society, **2018**, *140*, 13181-13184

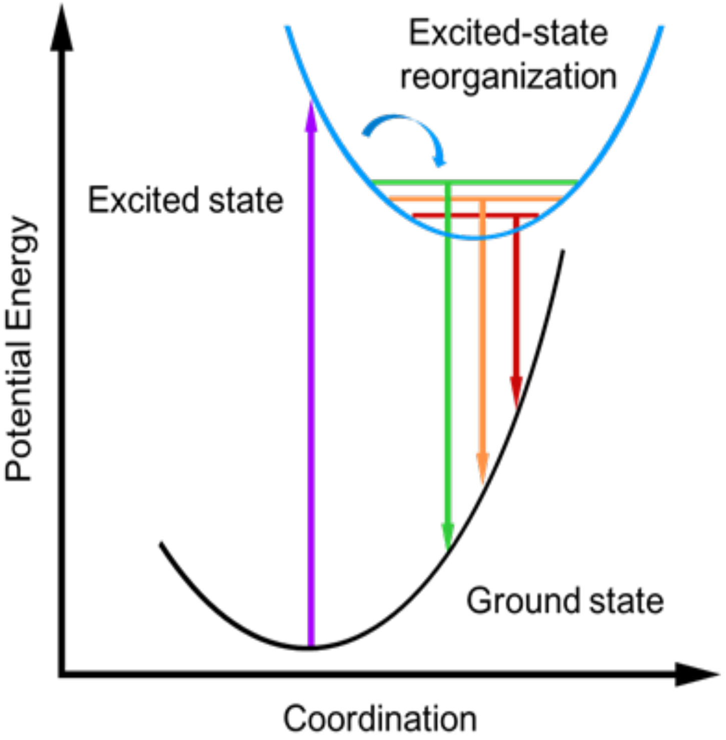
0D Organic Metal Halide Hybrids

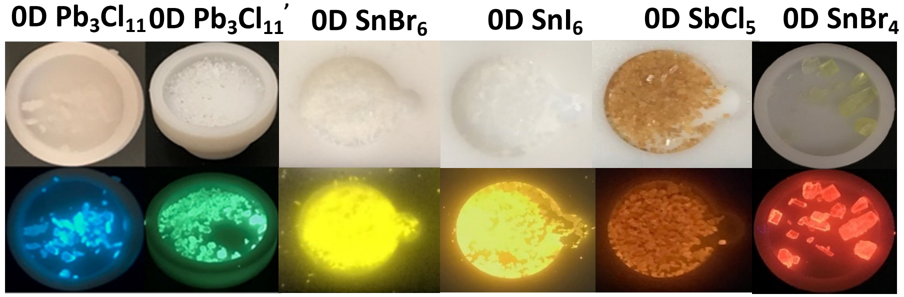


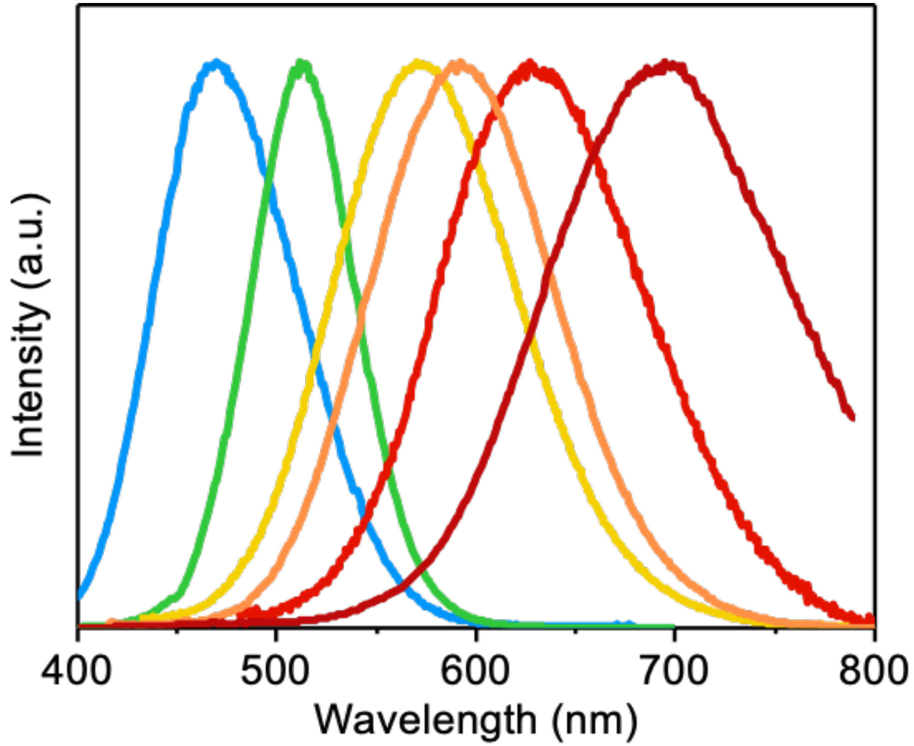
Perfect Host-Guest System





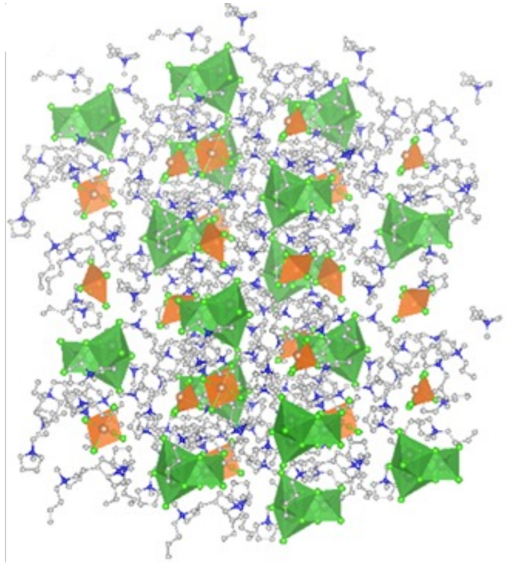


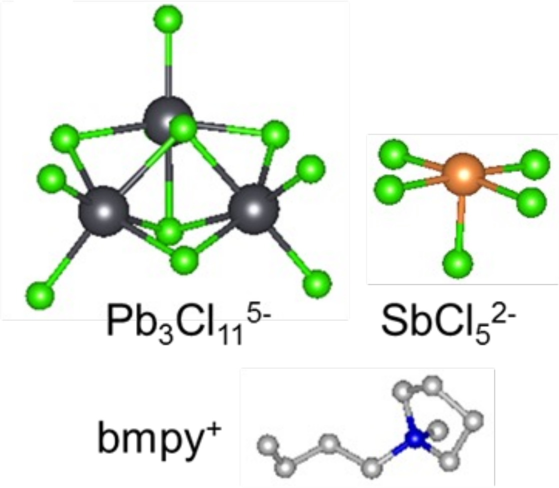


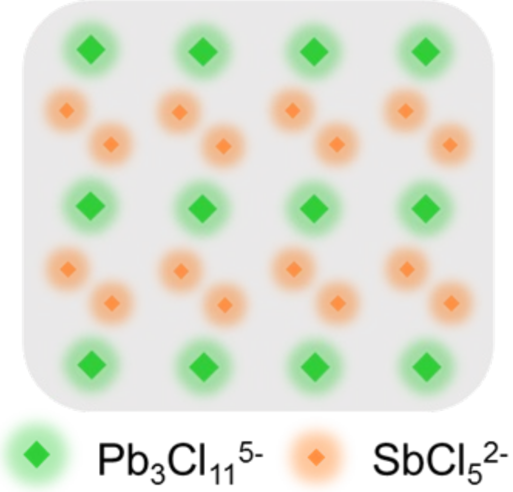


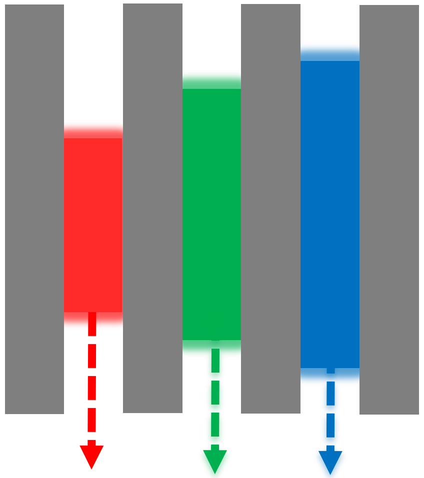
Chemical Science, **2018,** 9, 586-593; *JACS*, **2018**, *140*, 13181-13184; *Angew. Chem. Int. Ed.*, **2017**, 56, 9018-9022; **2018**, 57, 1021-1024; **2020**, *59*, 14120-14123; *ACS Energy Letters*, **2018**, *3*, 54-62; **2018**, *3*, 1443-1449; **2019**, *4*, 1579-1583; *ACS Materials Letters*, **2019**, *1*, 594-498; **2020**, *2*, 376-380; **2020**, *2*, 633-638; *Chemistry of Materials*, **2018**, *30*, 2374-2378; **2020**, *32*, 374-380

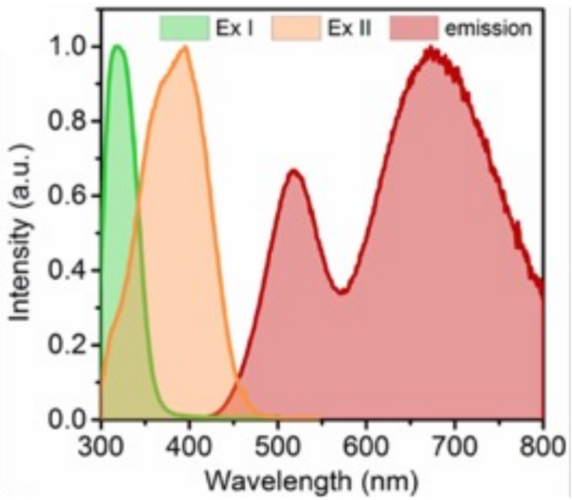
Multicomponent Systems (I)

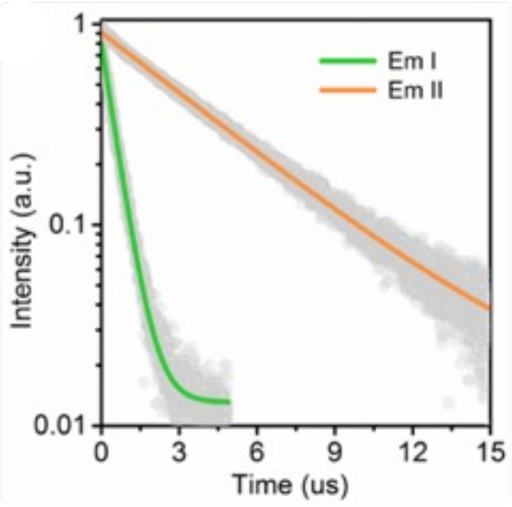


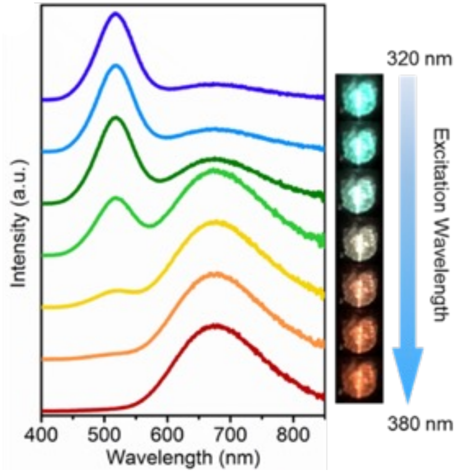






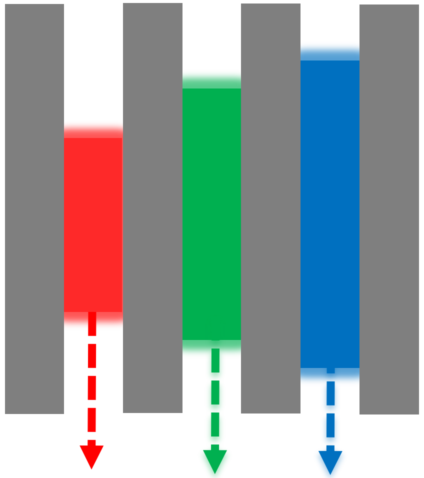


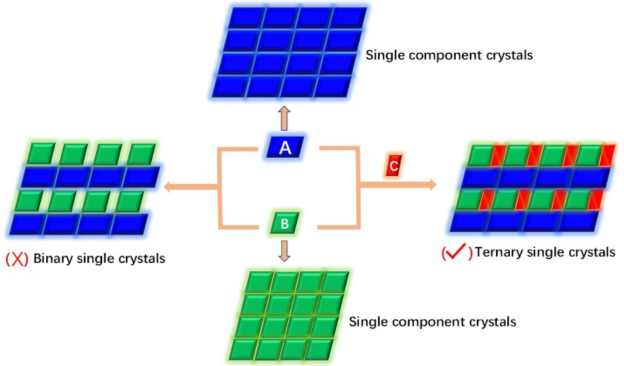


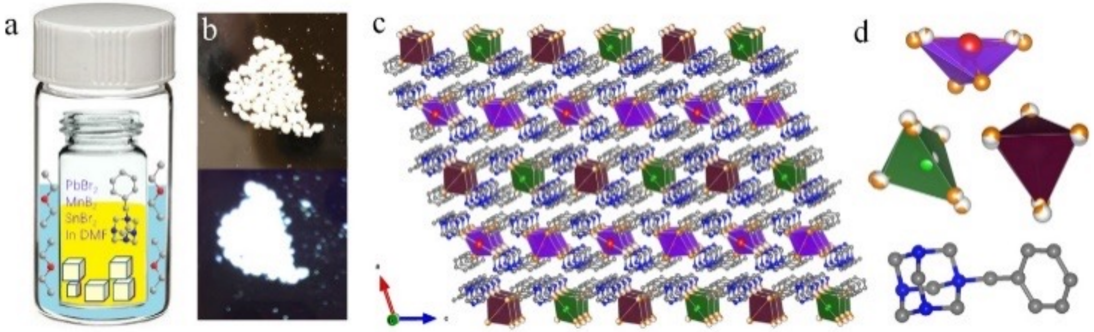


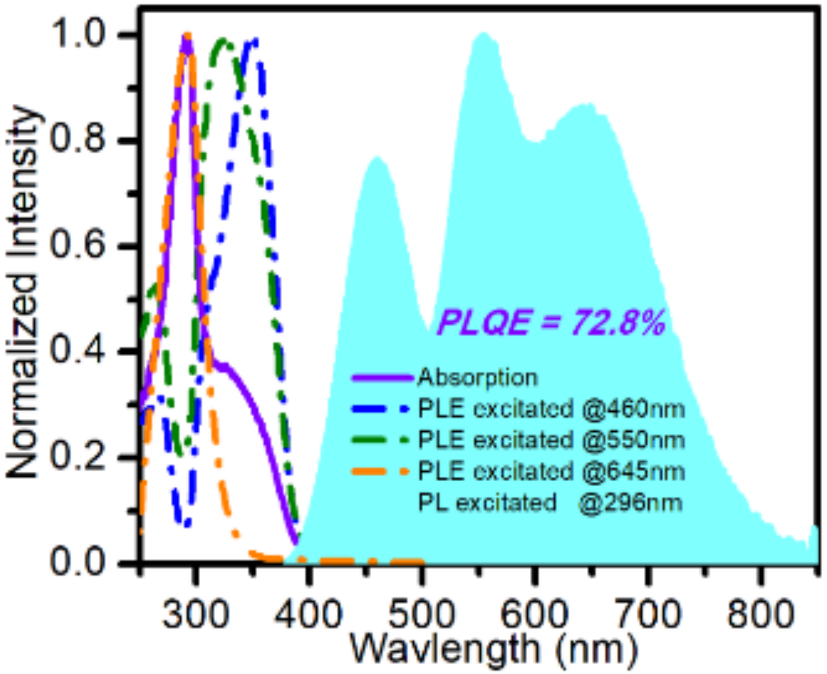
ACS Materials Letters, **2020**, *2*, 376-380

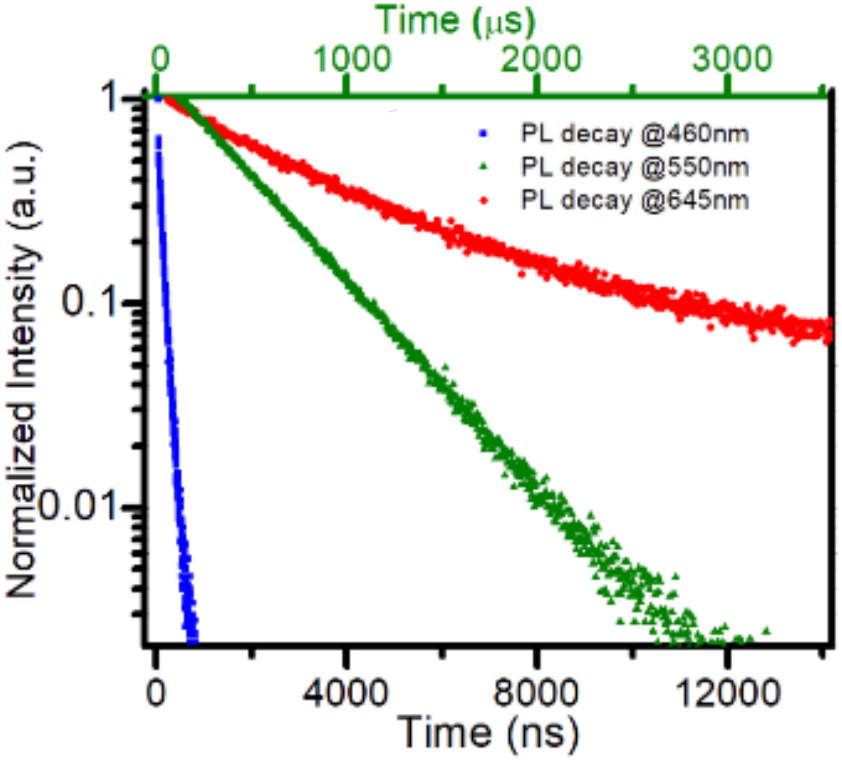
Multicomponent Systems (II)







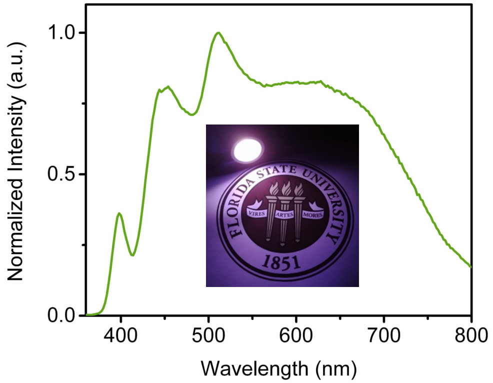


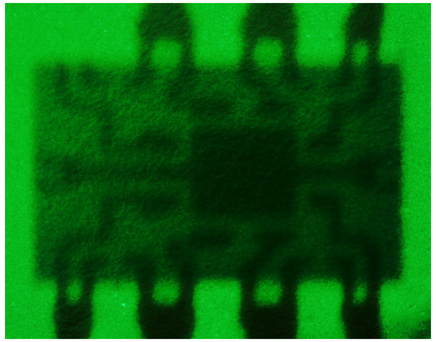


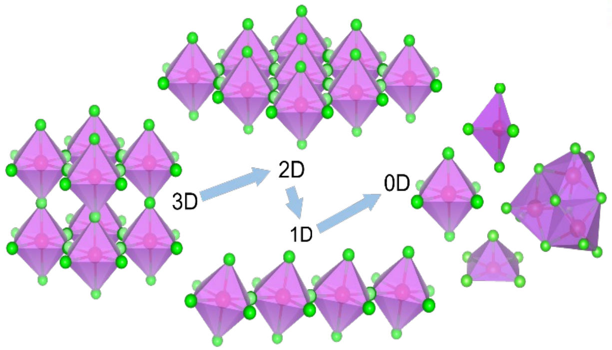
Angewandte Chemie International Edition, **2020**, *59*, 14120-14123

MA·GROUP
Advanced Materials for Electronics & Energy Devices

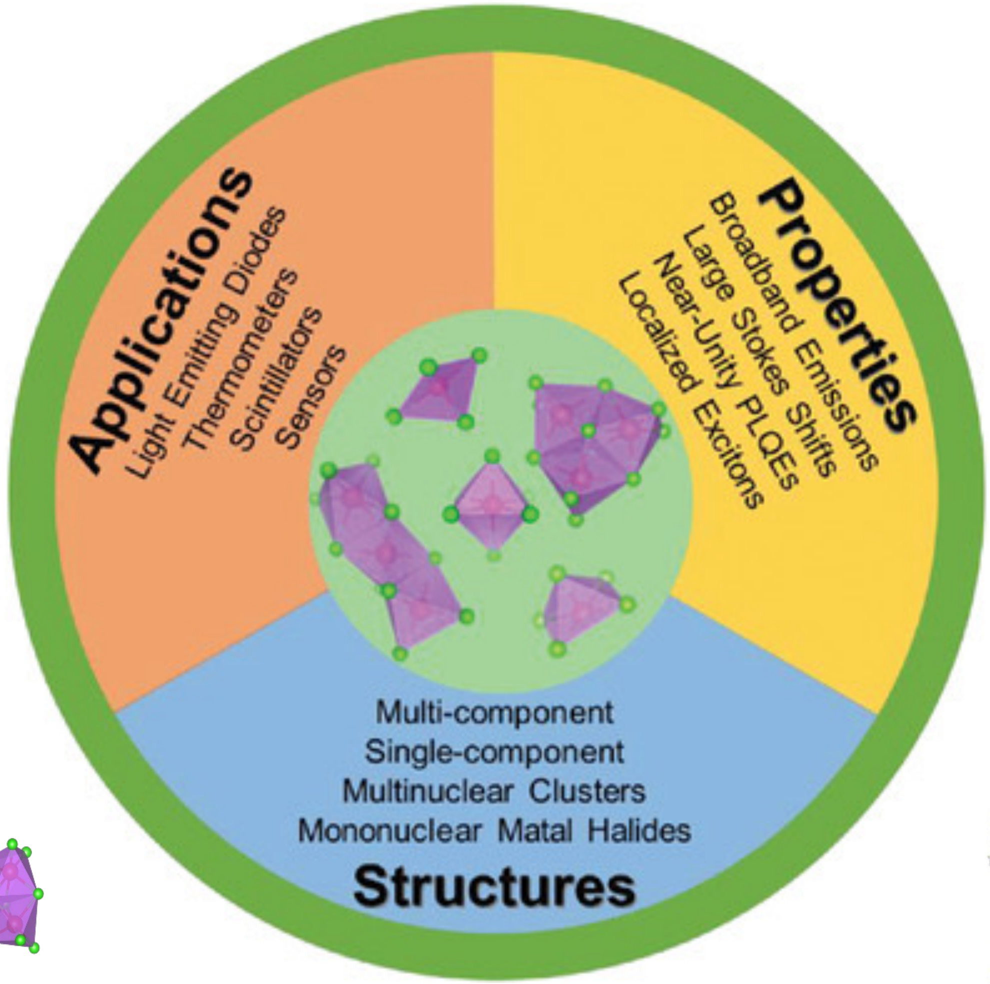
0D Organic Metal Halide Hybrids

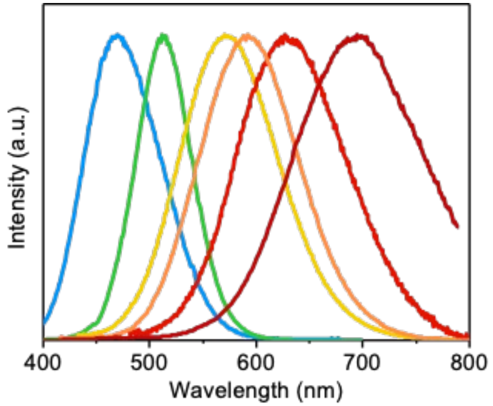


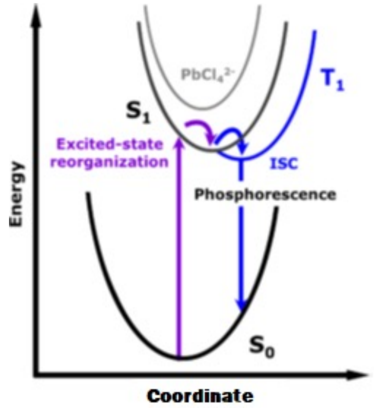


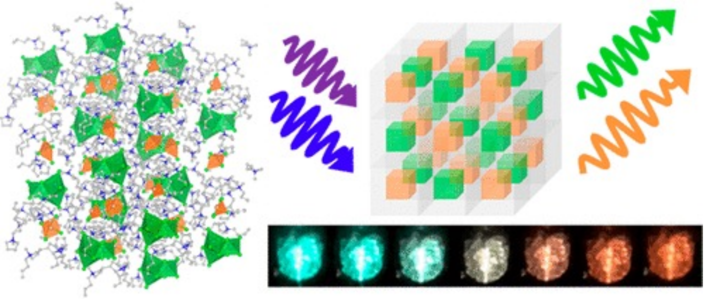


Recent Advances in Luminescent
Zero-Dimensional Organic Metal Halide Hybrids



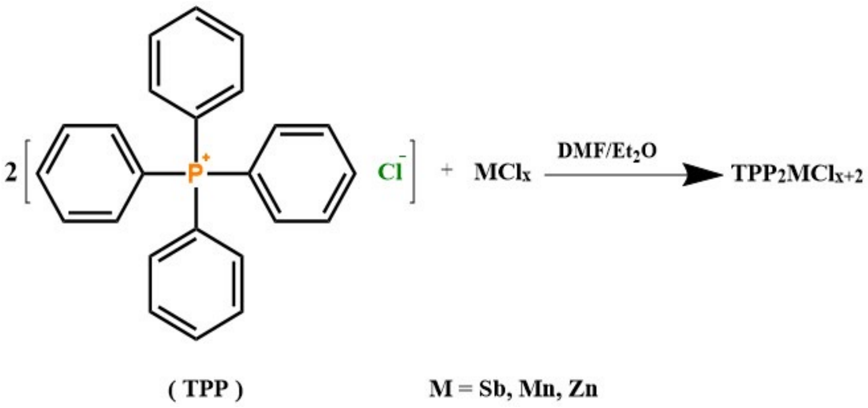


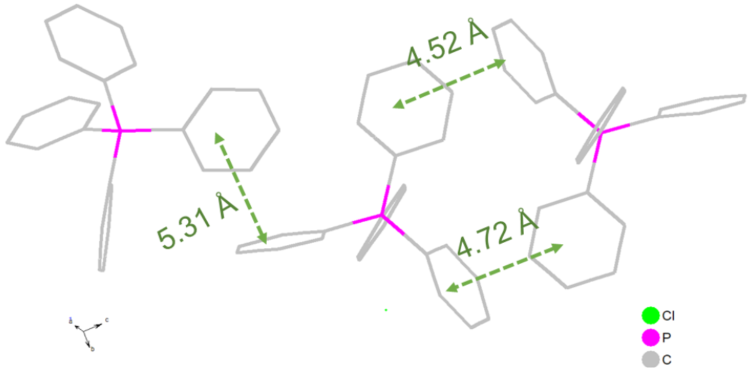


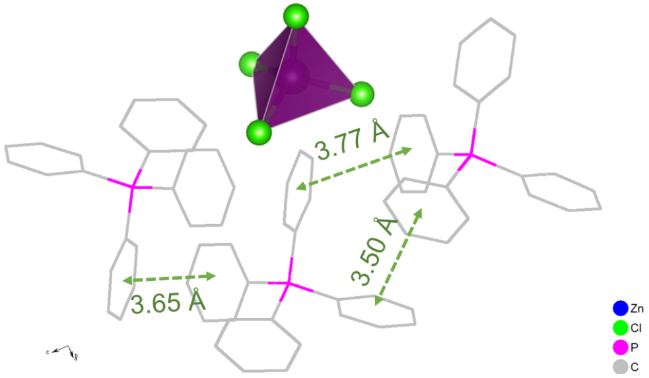


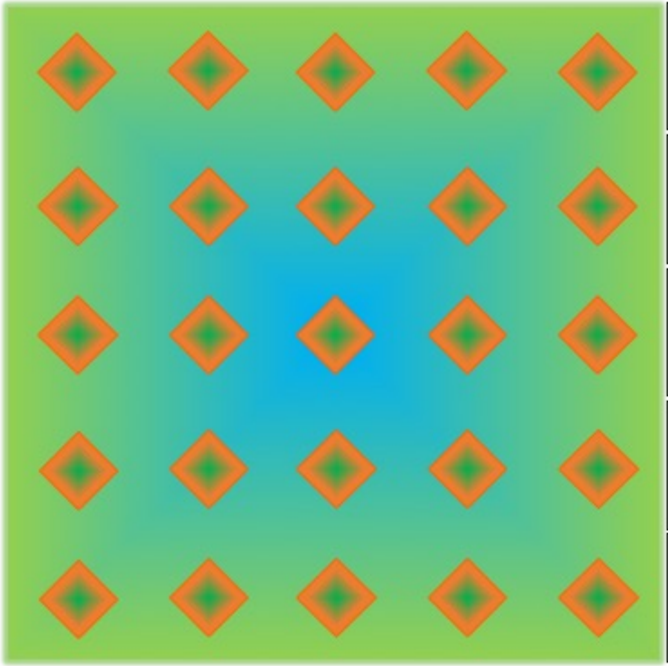
Advanced Optical Materials, **2021**, *9*, 2001766

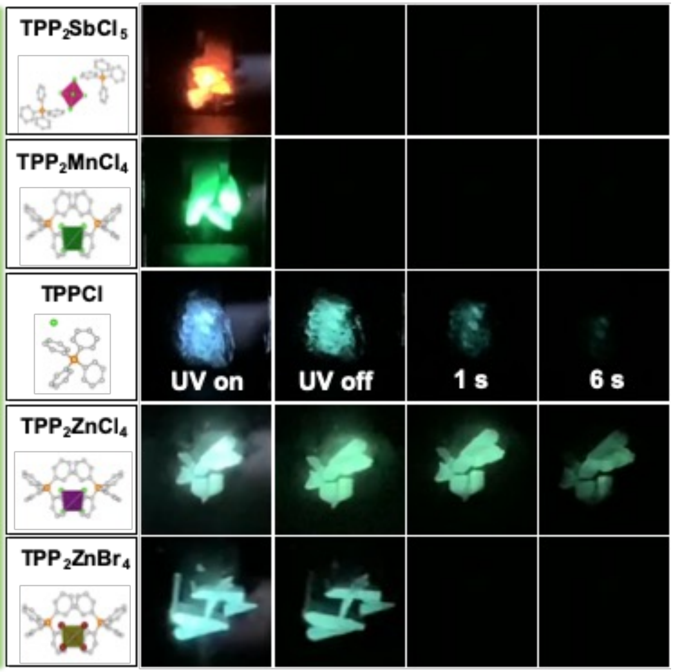
Metal Halides as Regulator

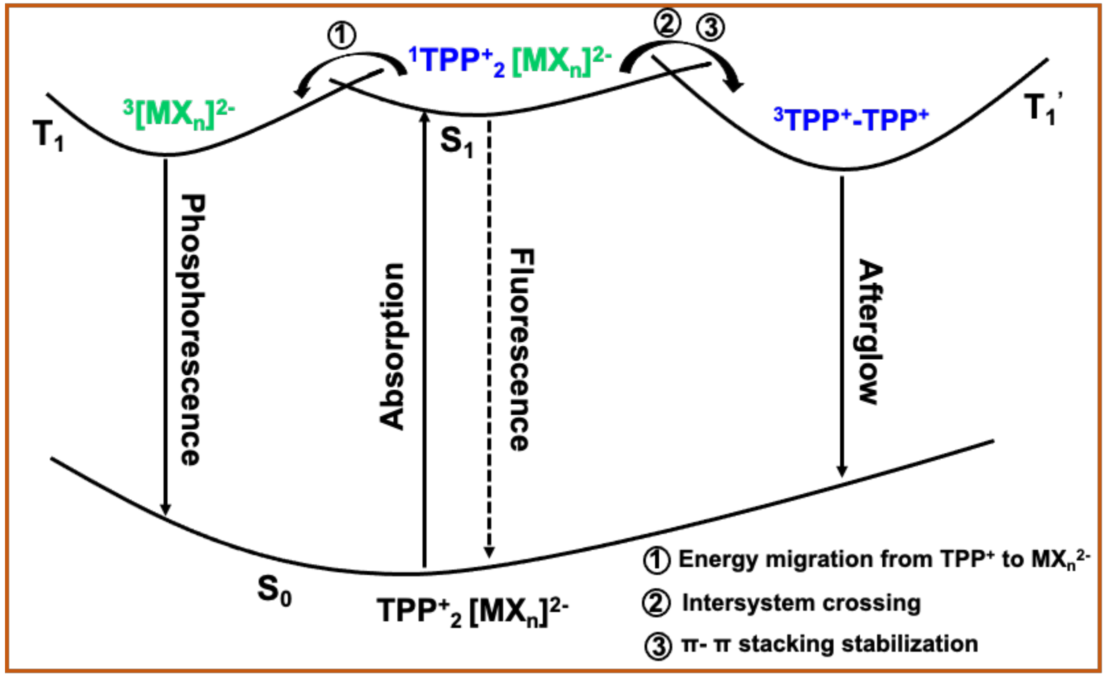






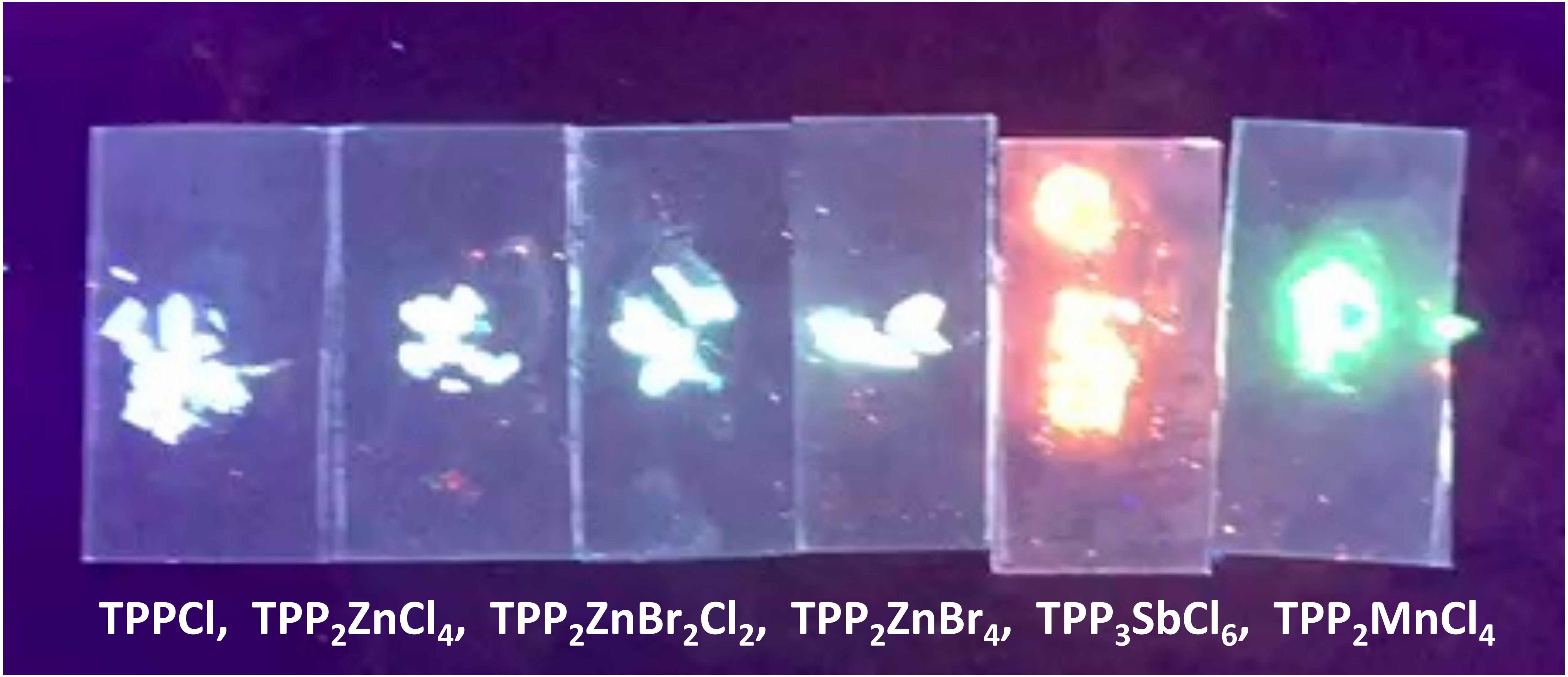






Angewandte Chemie International Edition, **2020**, *59*, 23067-23071

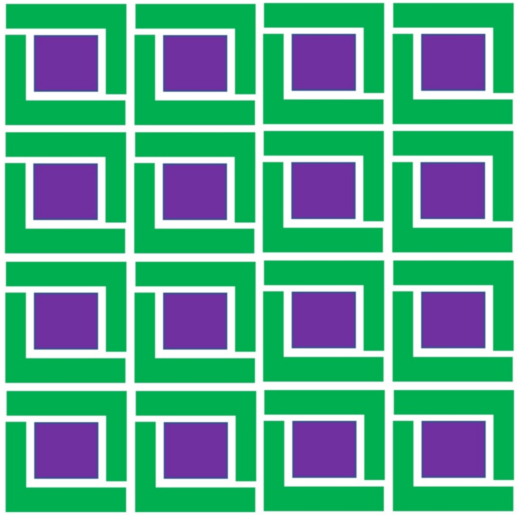
Tetraphenylphosphonium Metal Halides

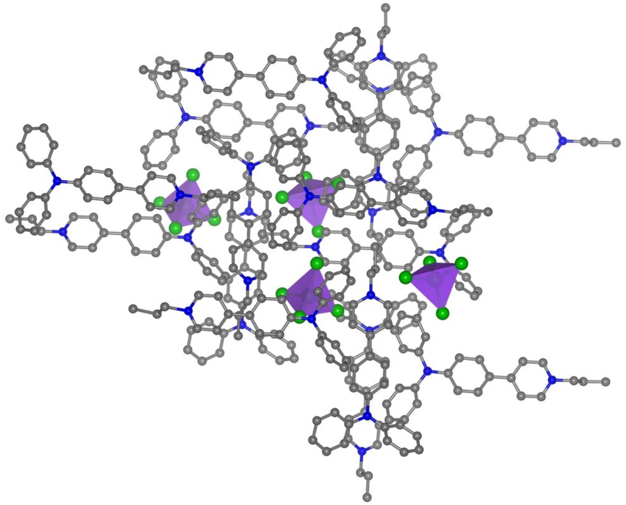


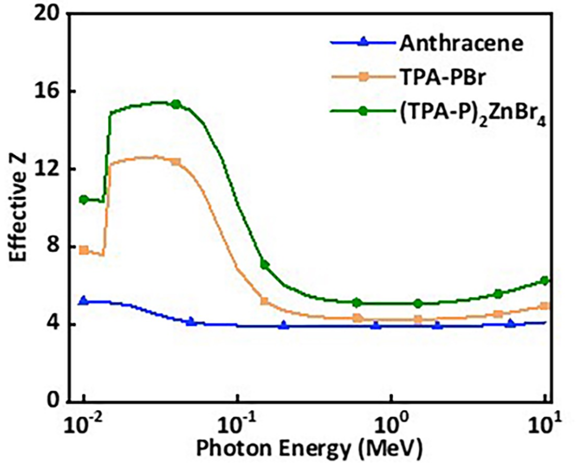
Angewandte Chemie International Edition, **2020,** *59*, 23067-23071

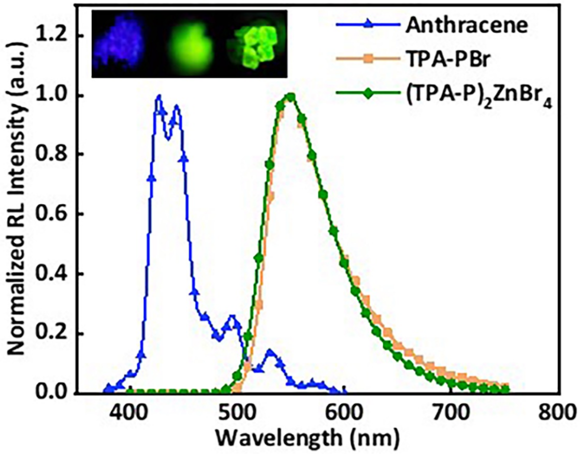
MA•GROUP
Advanced Materials for Electronics & Energy Devices

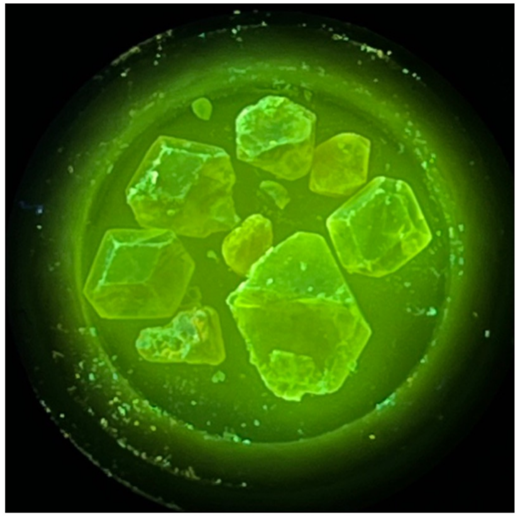
Metal Halides as Sensitizer

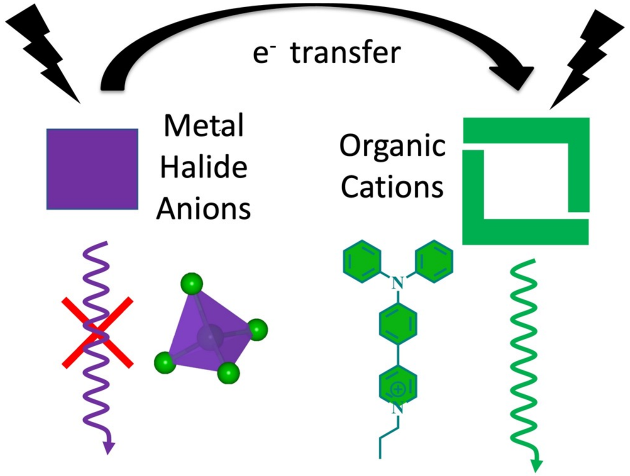


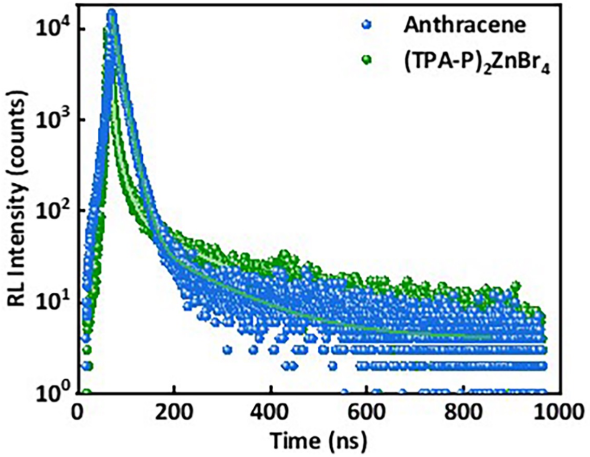


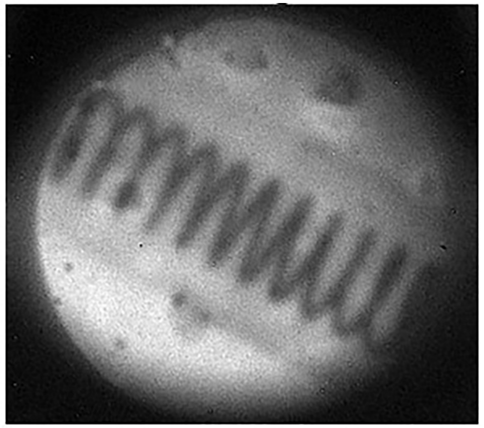










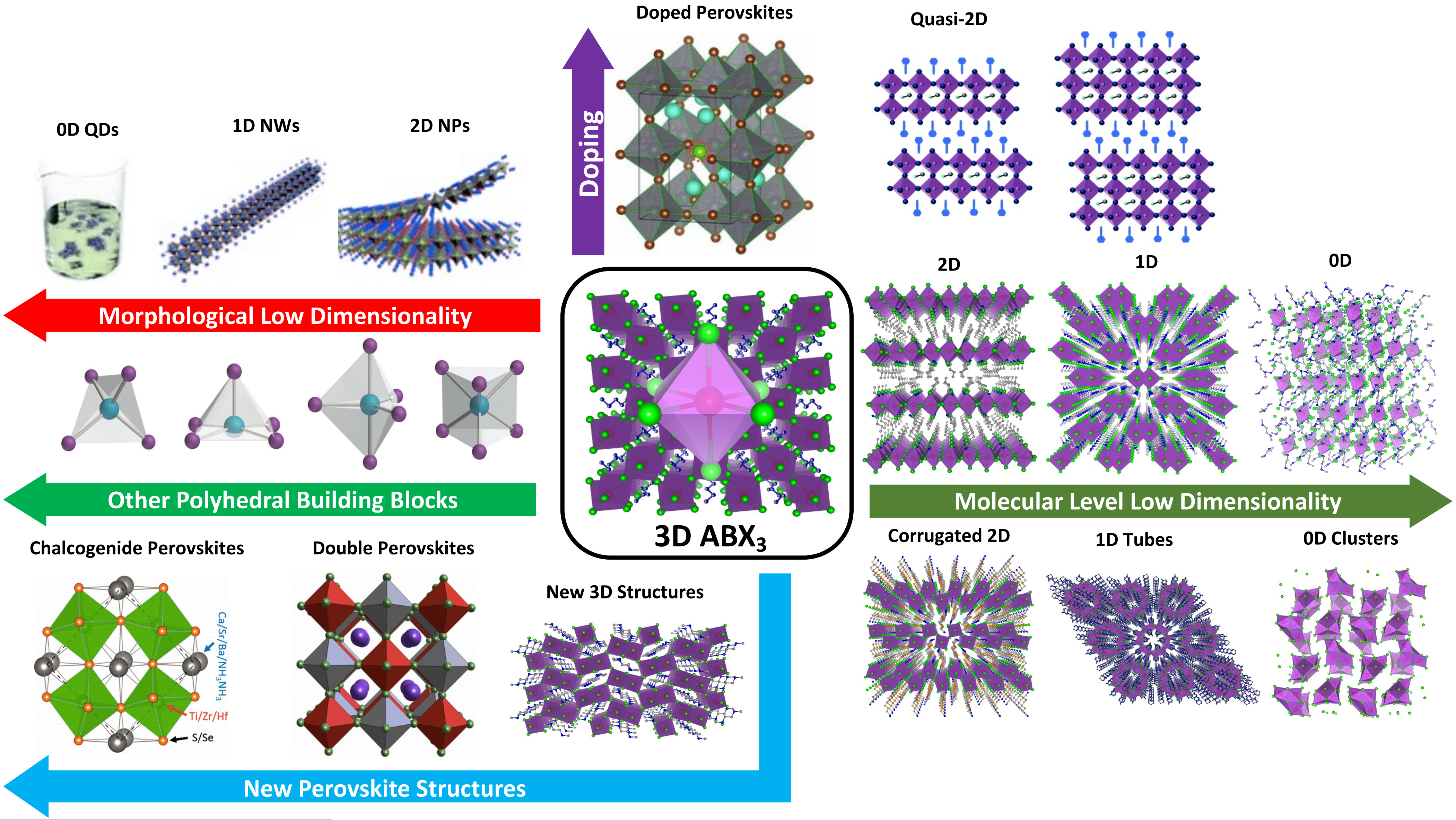


Advanced Materials, **2023,** 2301612

Conclusions

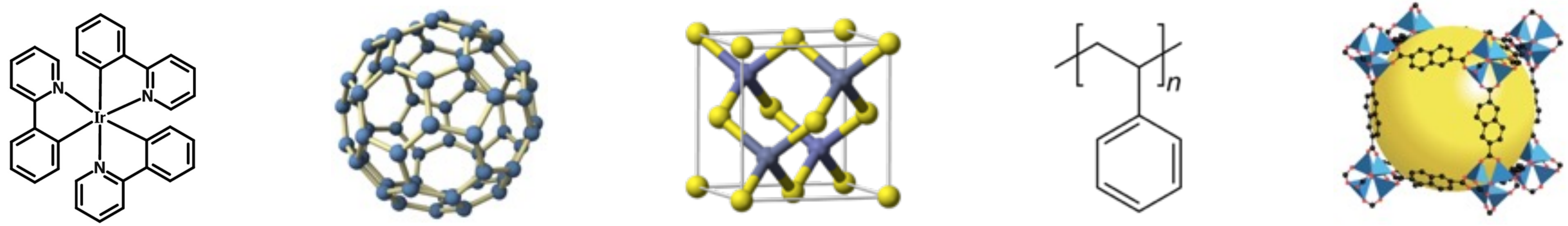
- Precise synthetic control has been achieved for the preparation of 1D and 0D organic metal halide hybrids.
- Understanding of the photoluminescence mechanisms has been achieved for organic metal halide hybrids with different dimensionalities at the molecular level.
- Multicomponent organic metal halide hybrids have been developed via proper crystal engineering.
- Photophysical tuning of 0D organic metal halide hybrids from phosphorescence to ultralong afterglow has been achieved by controlling the metal halides.
- Using metal halides and many other complex species as counter ions to co-crystallize with organic ions to form ionically bonded systems has remarkable potential to deliver new functional materials.

Perovskites and Beyond

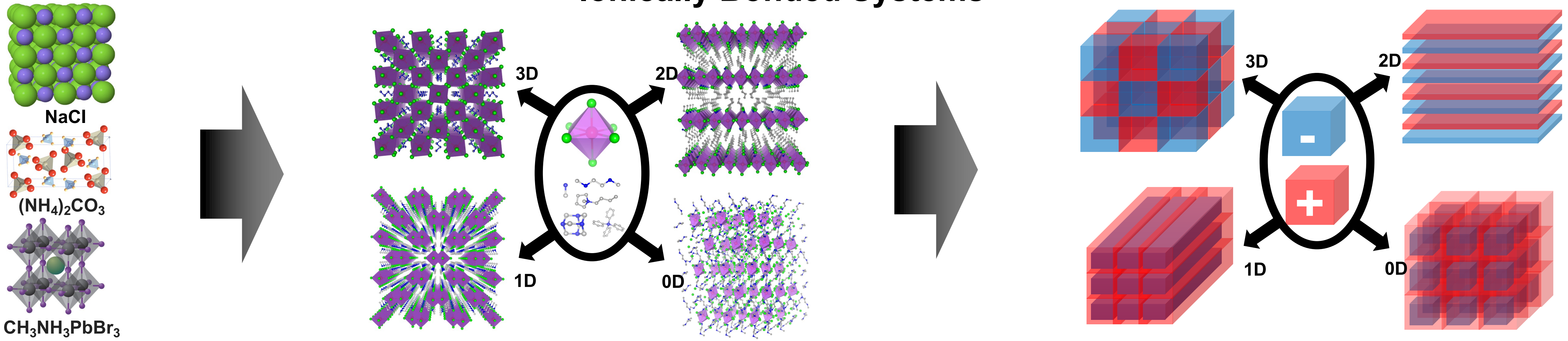


Organic-Inorganic Hybrids

Covalently Bonded Materials



Ionically Bonded Systems



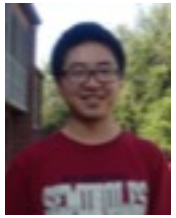
There is a vast space to explore organic-inorganic hybrids beyond perovskites, and we expect to see a lot of new science.

MA·GROUP
Advanced Materials for Electronics & Energy Devices

Acknowledgements


Dr. Chenkun Zhou


Dr.Haoran Lin

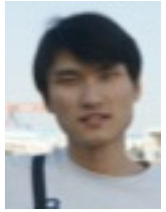

Dr. Yu Tian


Dr. Zhao Yuan


Dr. Michael Worku


Tunde Shonde


Dr. Liangjin Xu


Dr. Qingquan He


Sujin Lee


Maya Chaaban


Azza Akacha


He Liu


Dr. Theo Siegrist


Dr. Hanwei Gao


Dr. Kenneth Hanson


Dr. Chen Huang

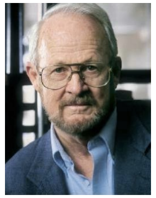

Dr. Michael Shatruk


Dr. Thomas E. Albrecht-Schmitt


Dr. Lei Zhu


Dr. Yanyan Hu


Dr. Joseph Schlenoff


Dr. Ronald Clark


Dr. Lina Cui


Dr. Lin X. Chen


Dr. Maohua Du


Dr. Yingzhong Ma


Dr. Jiangeng Xue


Dr. Bumjoon Kim


Dr. Xiaobo Chen


Dr. Shangchao Lin


Dr. Kirk Schanze


Dr. Peter Djurovich


Dr. Liang Tan


Dr. Franky So


Dr. Daniel Dougherty


Dr. Xujie Lv

NSF

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
UNITED STATES AIR FORCE

FLORIDA STATE UNIVERSITY 1851