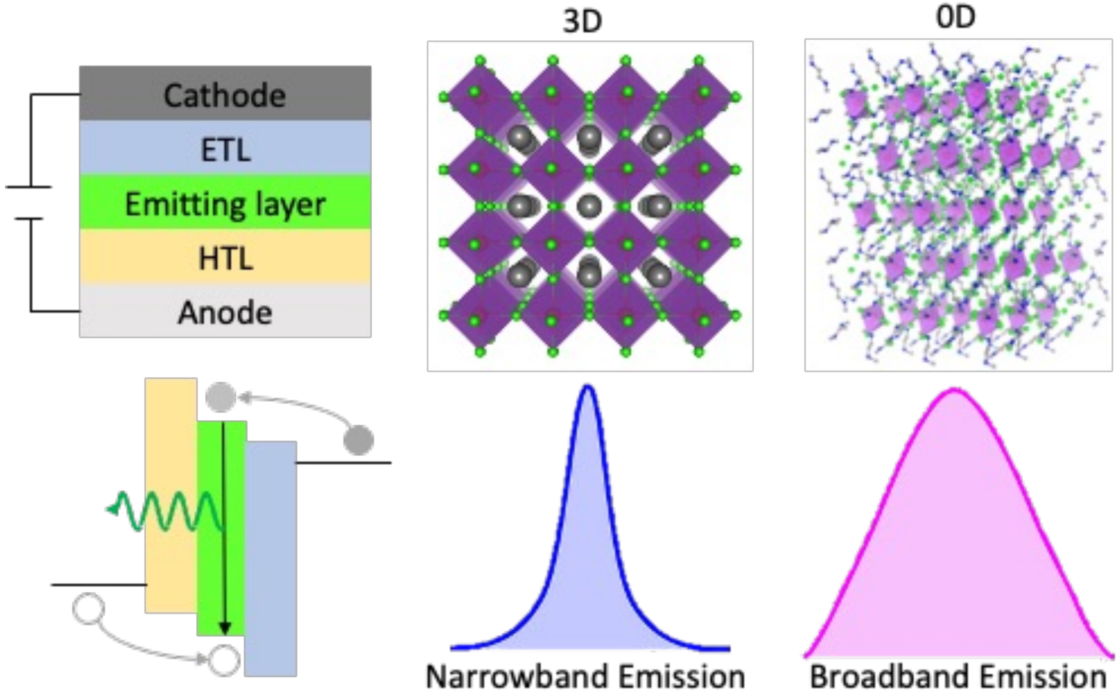
Light Emitting Diodes Based on Metal Halide Perovskites and Beyond



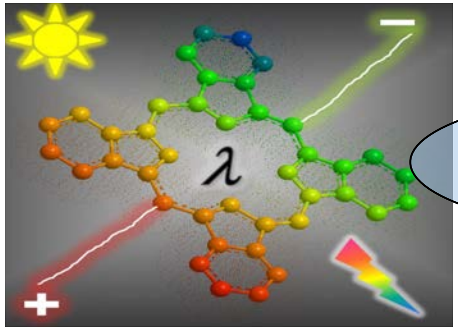
Biwu Ma

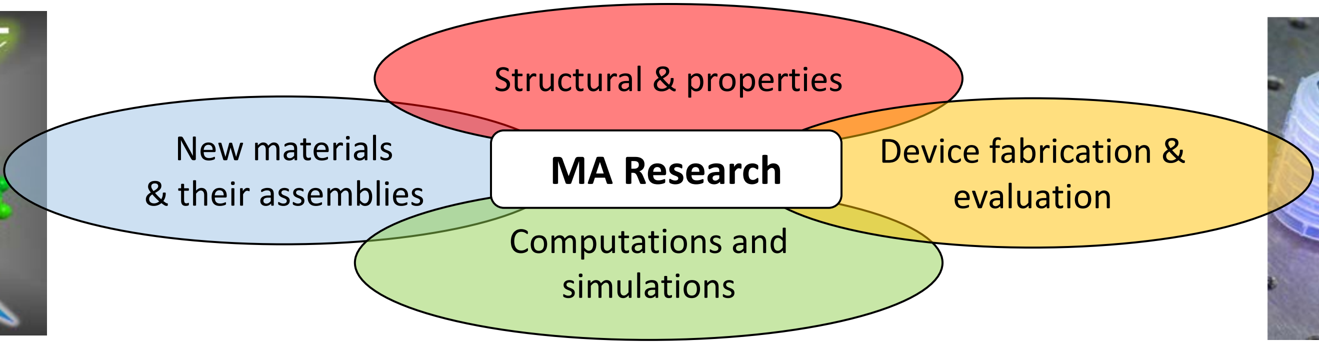
Florida State University

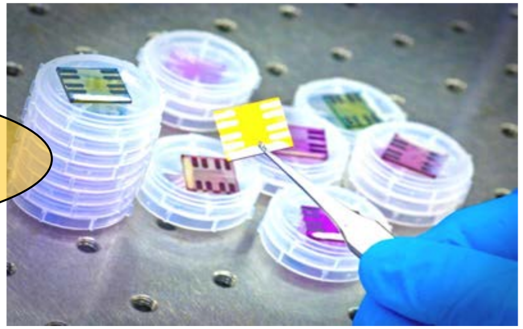
MA • GROUP
Advanced Materials for Electronic & Energy Devices

MA·GROUP
Advanced Materials for Electronics & Energy Devices

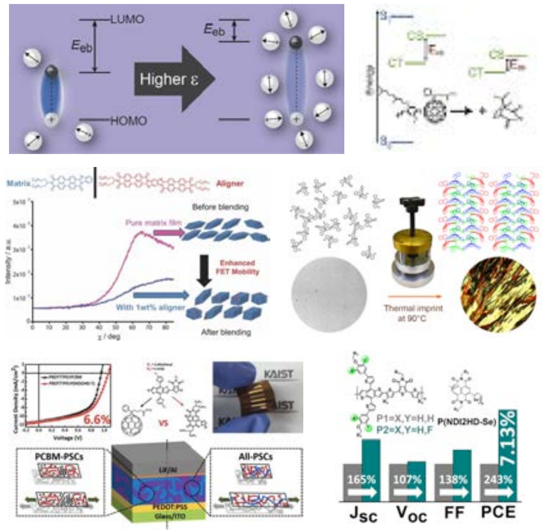
Ma Group @ FSU





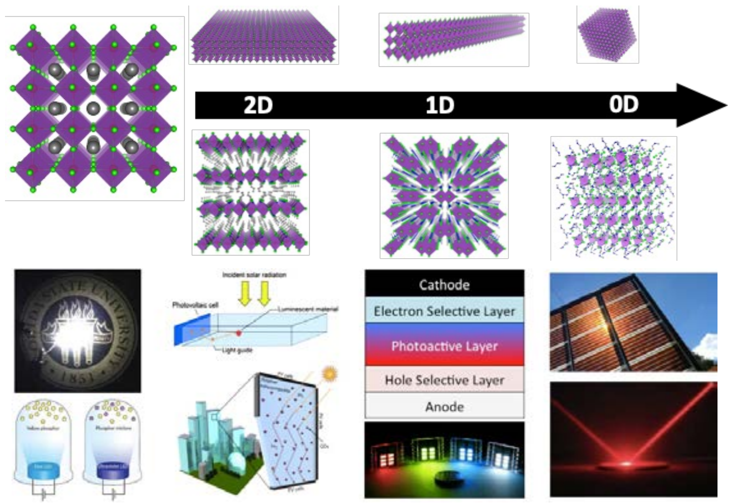


Organic Electronics



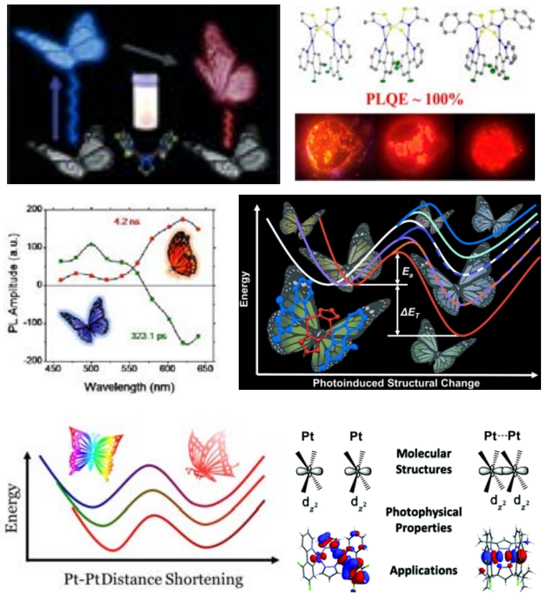
ACS Appl. Mater. Interfaces, **2013**, *5*, 10105-10110; *Advanced Functional Materials*, **2014**, *24*, 7588-7596; **2017**, *27*, 1703070; **2020**, *30*, 2005787; *The Journal of Physical Chemistry C*, **2017**, 121, 3279-3285. *Advanced Materials*, **2014**, *26*, 1223-1228; **2016**, *28*, 10016–10023; *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

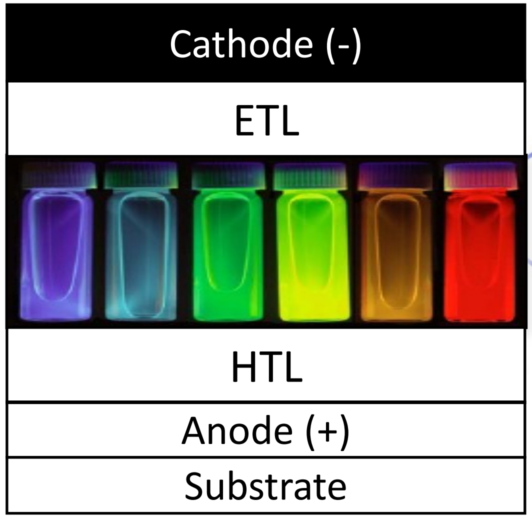


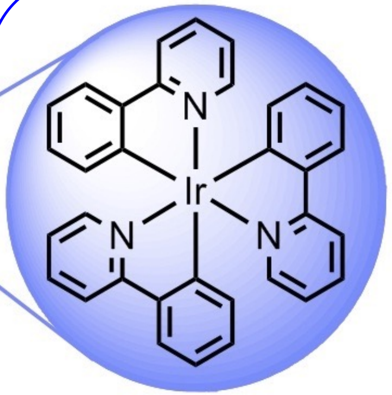
Angew. Chem. Int. Ed., **2014**, *53*, *10908-10912*; **2015**, *54*, *9591-9595*; *Inorg. Chem*, **2016**, *55*, 8564-8569; **2020**, *59*, 13109-13116; *Chemistry - A European Journal*, **2017**, 23, 1-7; *J. Mater. Chem. C*, **2019**, *7*, 5910—5924

Outline

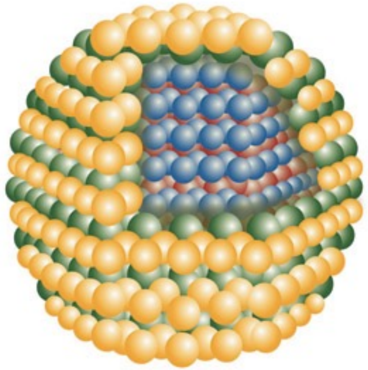
- **Introduction**
  - Thin Film Light Emitting Diodes (LEDs)
- **Metal Halide Perovskites**
  - Color Tuning of Metal Halide Perovskites
  - Blue LEDs Based on Metal Halide Perovskites
- **Organic Metal Halide Hybrids Beyond Perovskites**
  - Color Tuning of Organic Metal Halide Hybrids
  - Electroluminescence from Organic Metal Halide Hybrids
- **Conclusions**
- **Acknowledgement**

Thin Film LEDs

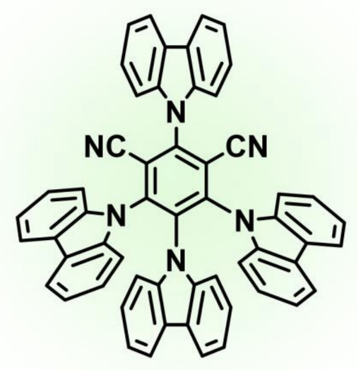




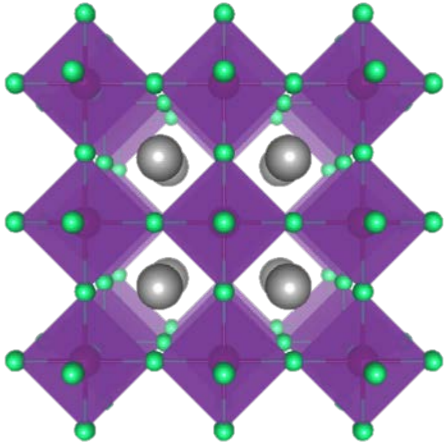
Phosphorescent Metal Complexes



Colloidal Quantum Dots



TADF Emitters



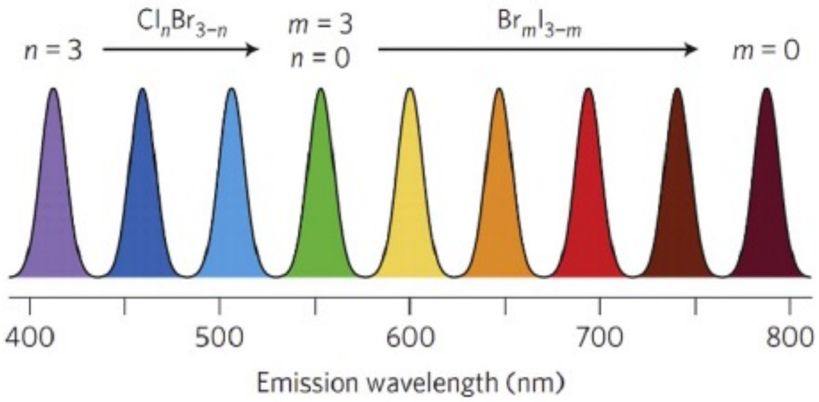
Metal Halide Perovskites

- Low-cost, earth-abundant
- Facile synthesis and preparation
- Low temperature processing
- Highly tunable band gaps
- Excellent charge transport
- Narrow emissions with high color purity

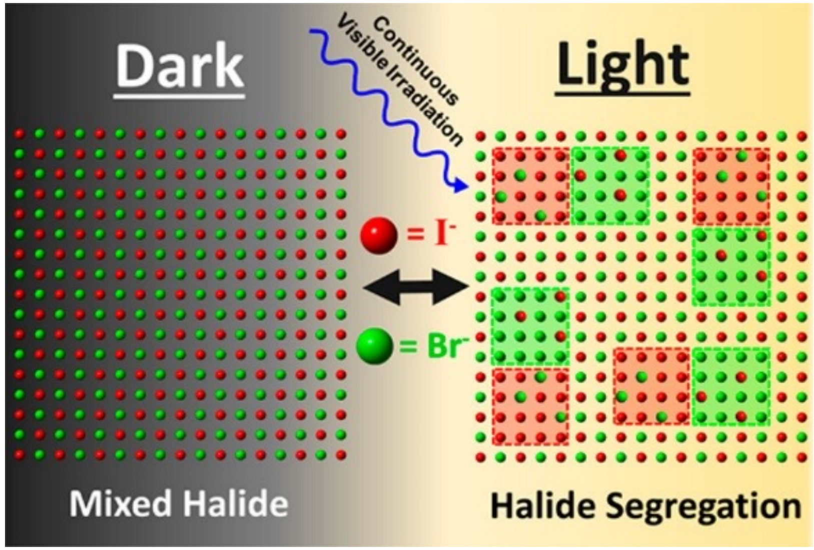
MA•GROUP
Advanced Materials for Electronics & Energy Devices

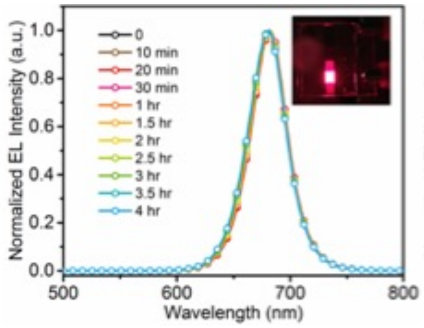
Color Tunability of Halide Perovskites

Compositional Modulation

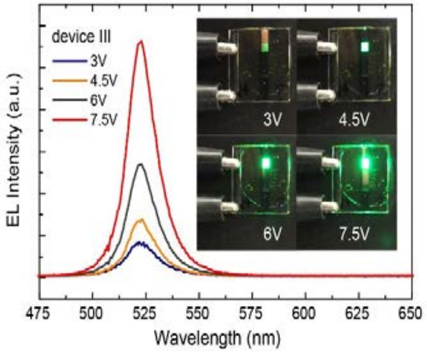


Nano Materials Science **2019**, *1*, 268–287
ACS Energy Lett. **2018**, *3*, 204–213

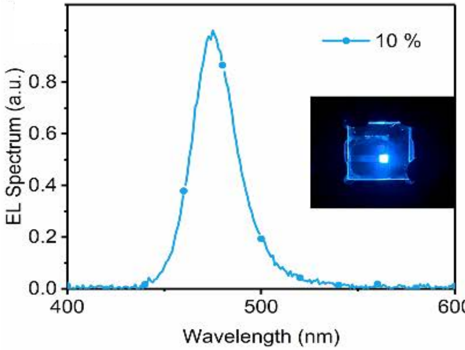




Advanced Materials, **2018**, *30*, 1707093

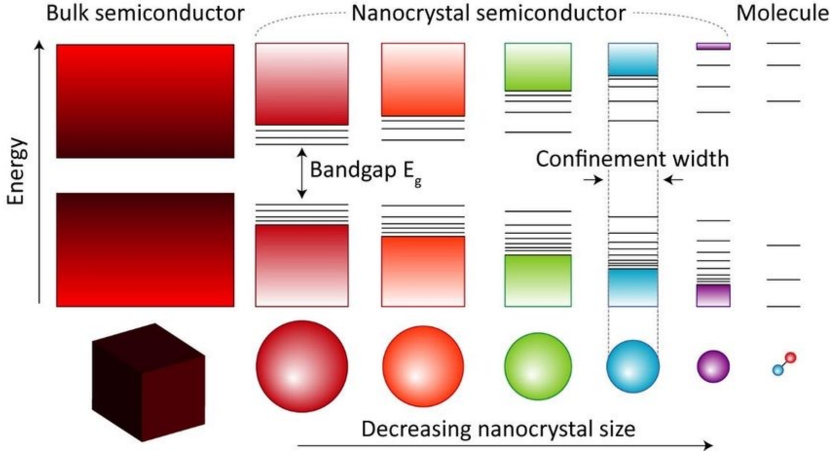


Advanced Materials, **2016**, *28*, 8983-8989

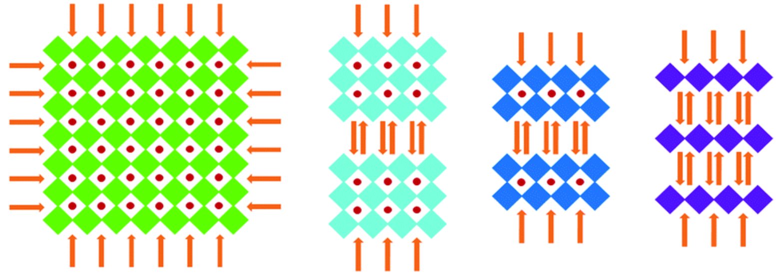


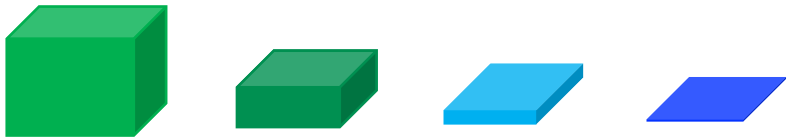
ACS AMI, **2020**, *12,* 45056-45063

Quantum Size Effects



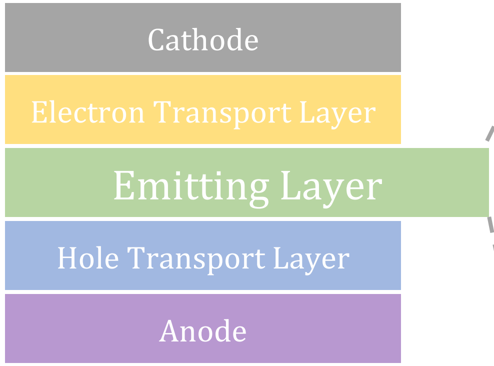
Topics in Current Chemistry **2016**, *374*, 58
Chemical Communications, **2016**, *52*, 3887-3890





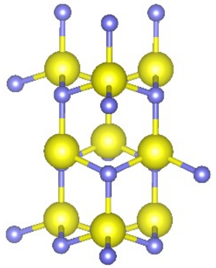
MA GROUP
Advanced Materials for Electronics & Energy Devices

PeLEDs: The Next Generation?



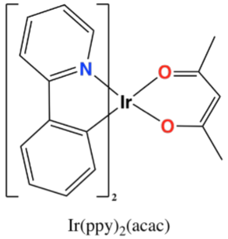
Small Science, **2021**,*1*, 2000072

III-V



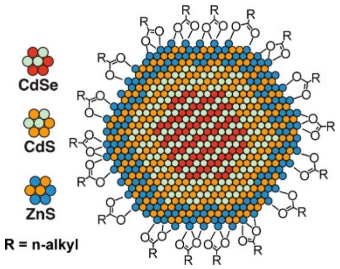
FWHM ~ 30 nm
- ✓ EQE > 20 %
- ✓ T_{50} > 100, 000 Hrs
- ✓ Commercialization: yes
- • Difficult to fabricate

OLED



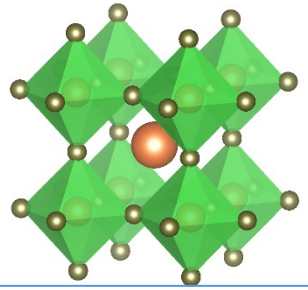
FWHM ~ 40 nm
- ✓ EQE > 20 %
- ✓ T_{50} > 100, 000 Hrs
- ✓ Commercialization: yes

QDLED

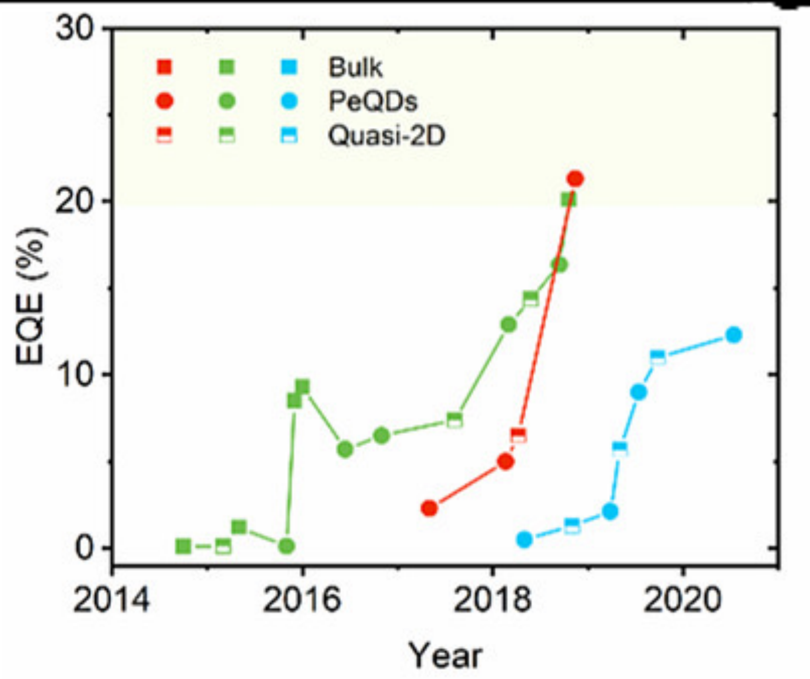


FWHM ~ 30 nm
- ✓ EQE > 20 %
- ✓ T_{50} > 100, 000 Hrs
- • Commercialization: No

PeLED



FWHM ~ 20 nm
- ✓ EQE > 20 %
- • T_{50} < 100, 000 Hrs
- • Commercialization: No



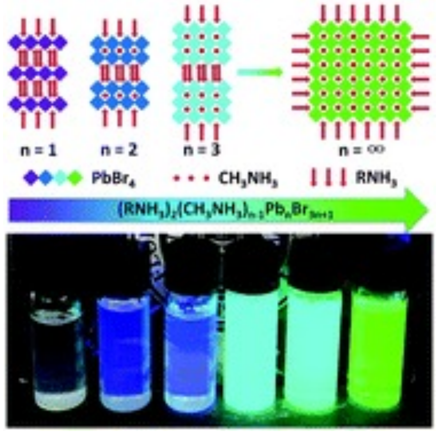
Some Issues and Challenges:

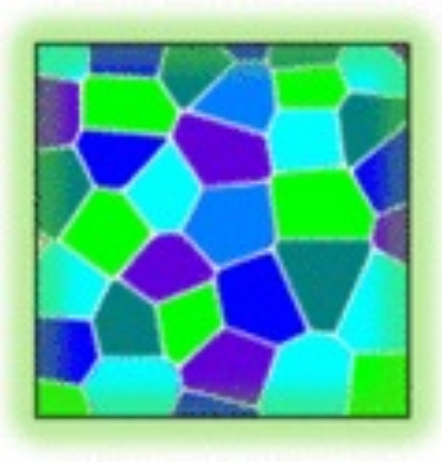
- Low stability of materials and devices
- Low performance of blue PeLEDs
- Processing and patterning
- Lead toxicity

MA·GROUP
Advanced Materials for Electronics & Energy Devices

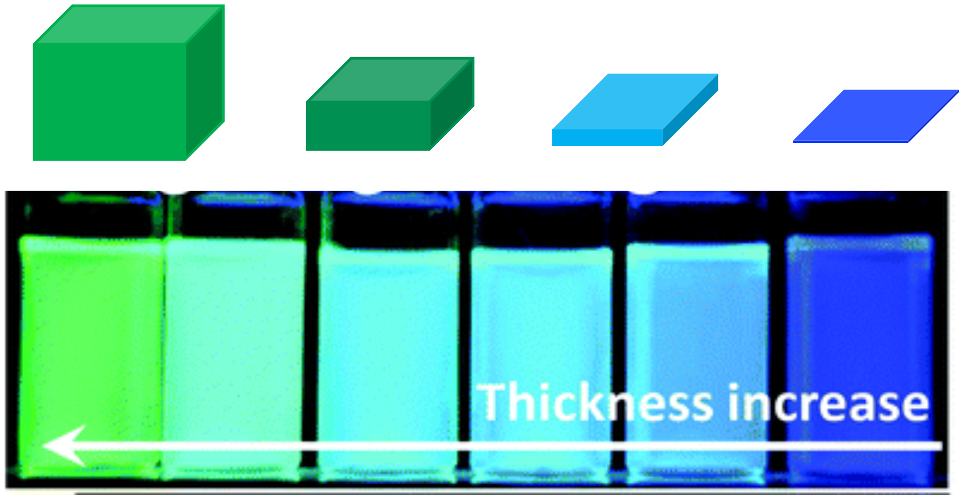
Blue Perovskite Emitters

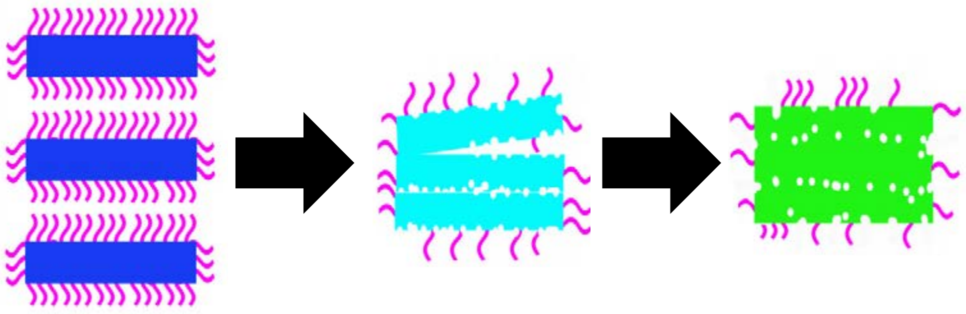
Quasi-2D Lead Bromide Perovskites

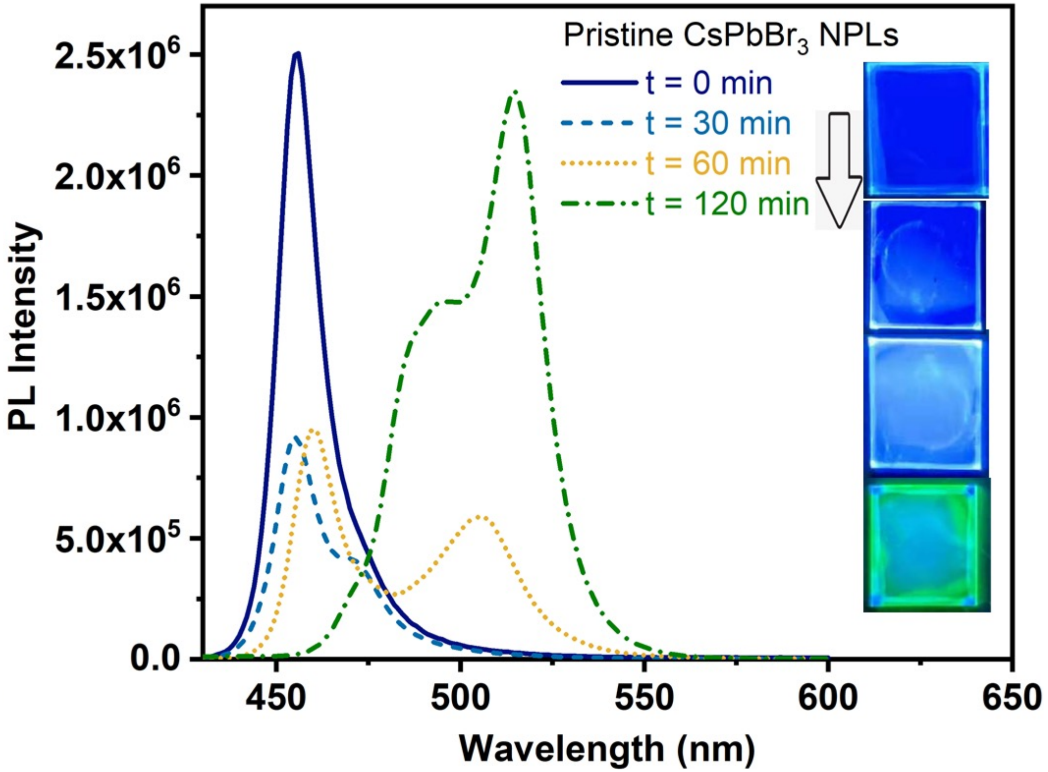




$CsPbBr_3$ Perovskite Nanoplatelets (NPLs)



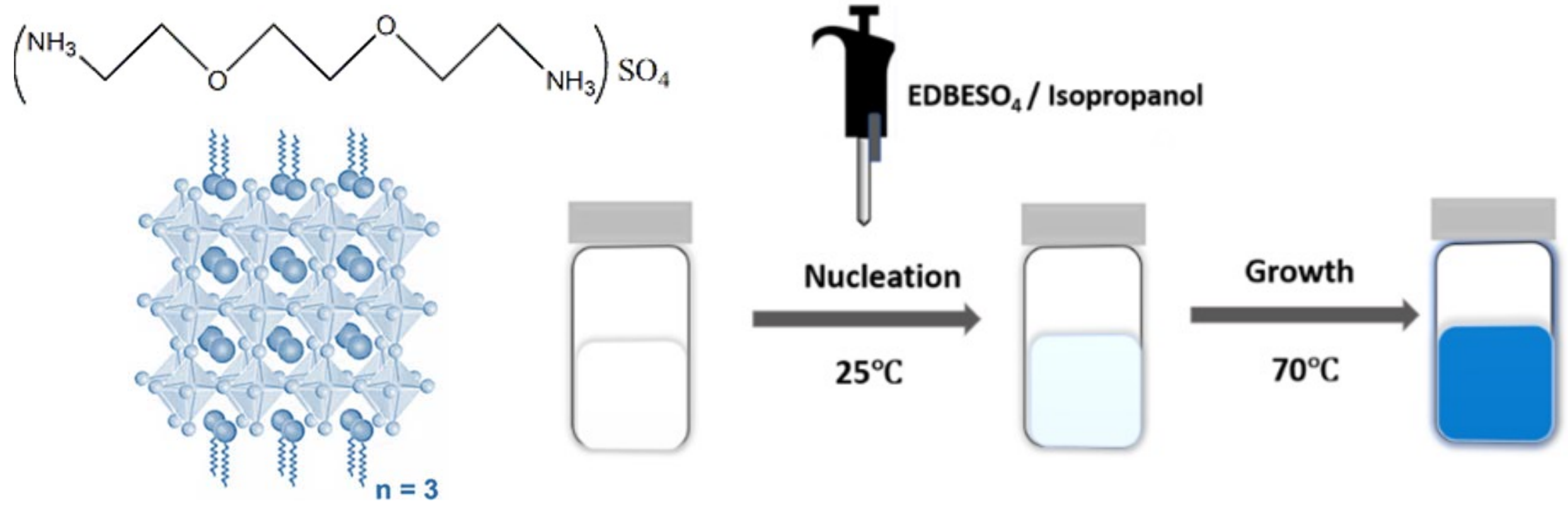


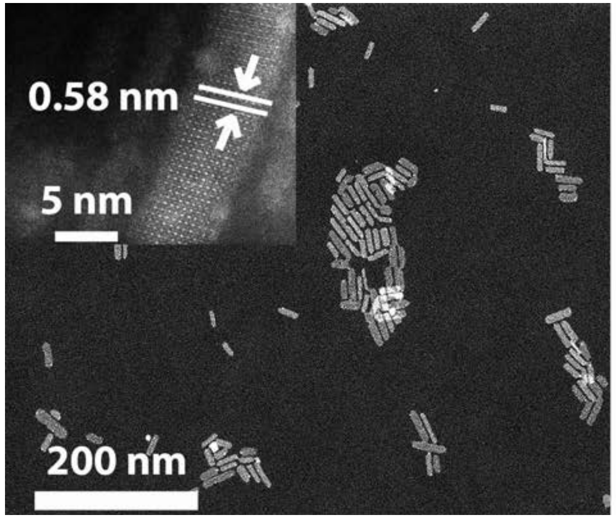


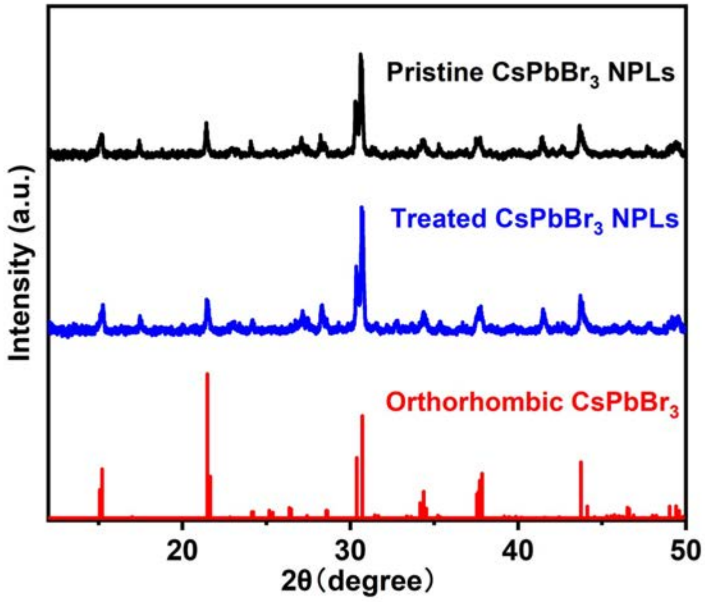
Chemical Communications, **2016**, *52*, 3887-3890; *Nano Letters* **2018**, *18*, 5231-5238; *ACS Appl. Mater. Interfaces* **2020**, *12*, 45056–45063; *ACS Energy Letters* **2020**, *5*, 1900-1907

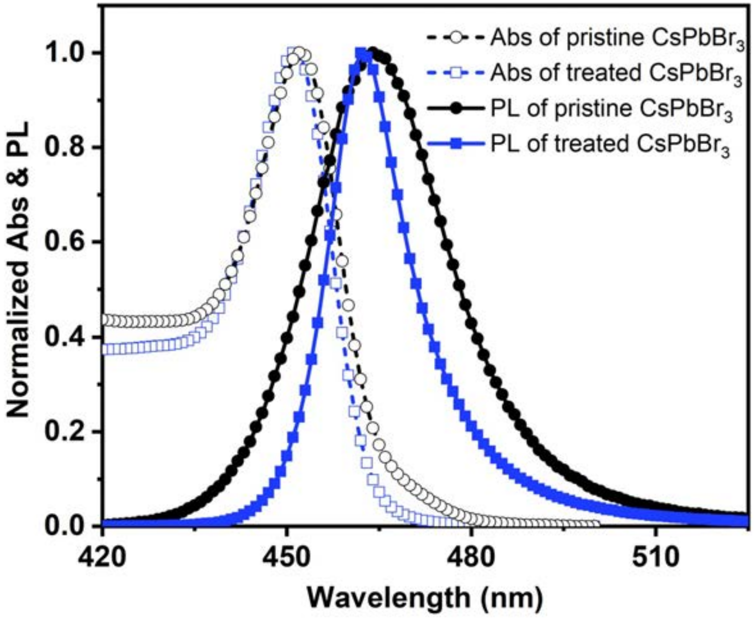
MA • GROUP
Advanced Materials for Electronics & Energy Devices

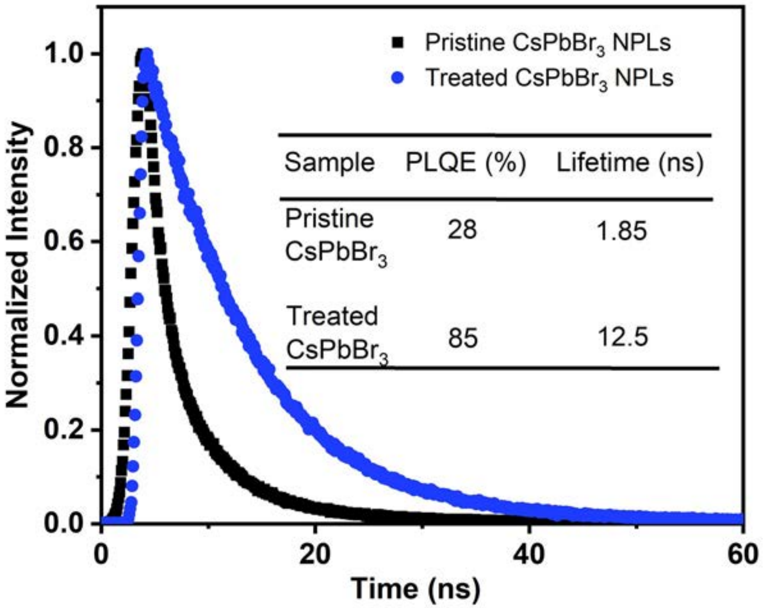
Organic Sulfate Treated $CsPbBr_3$ NPLs





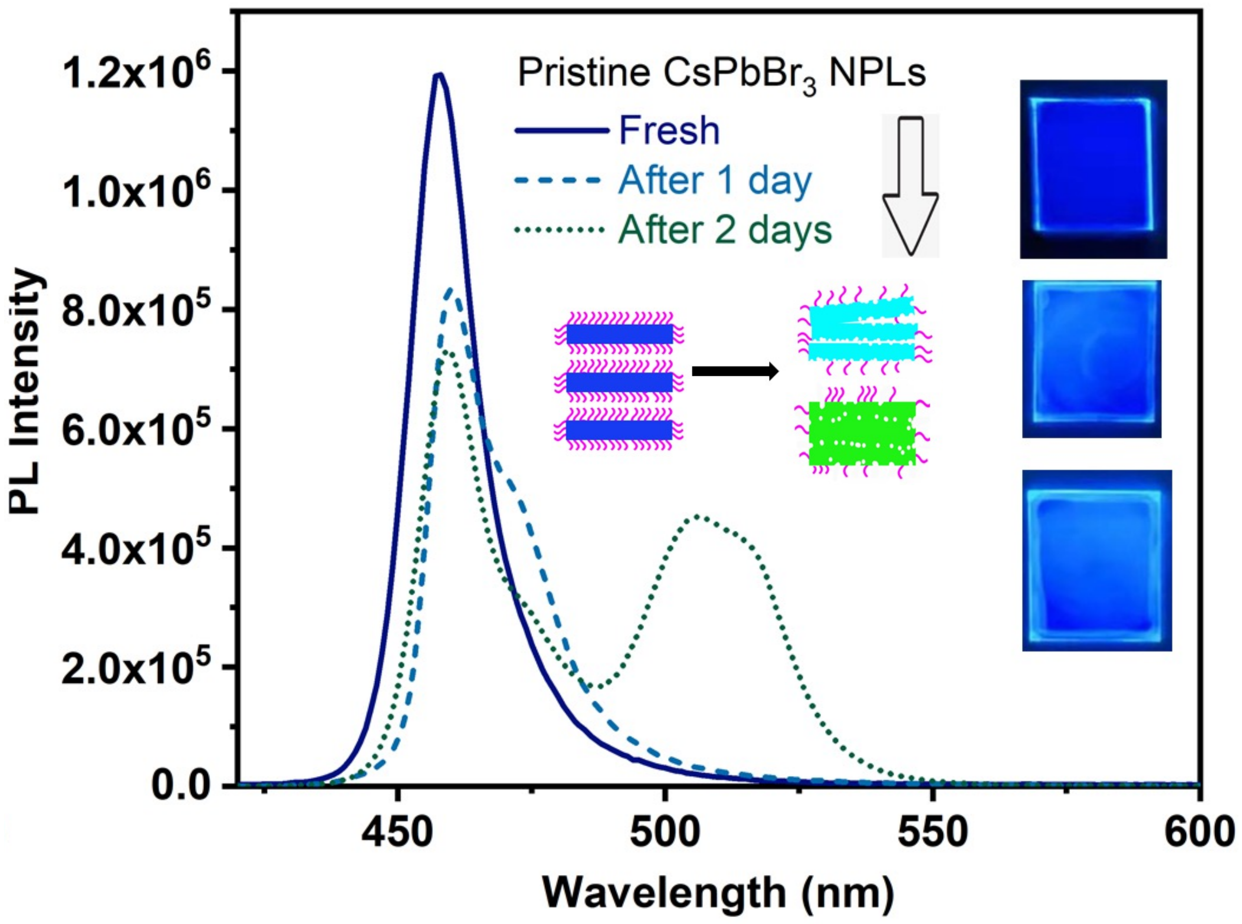


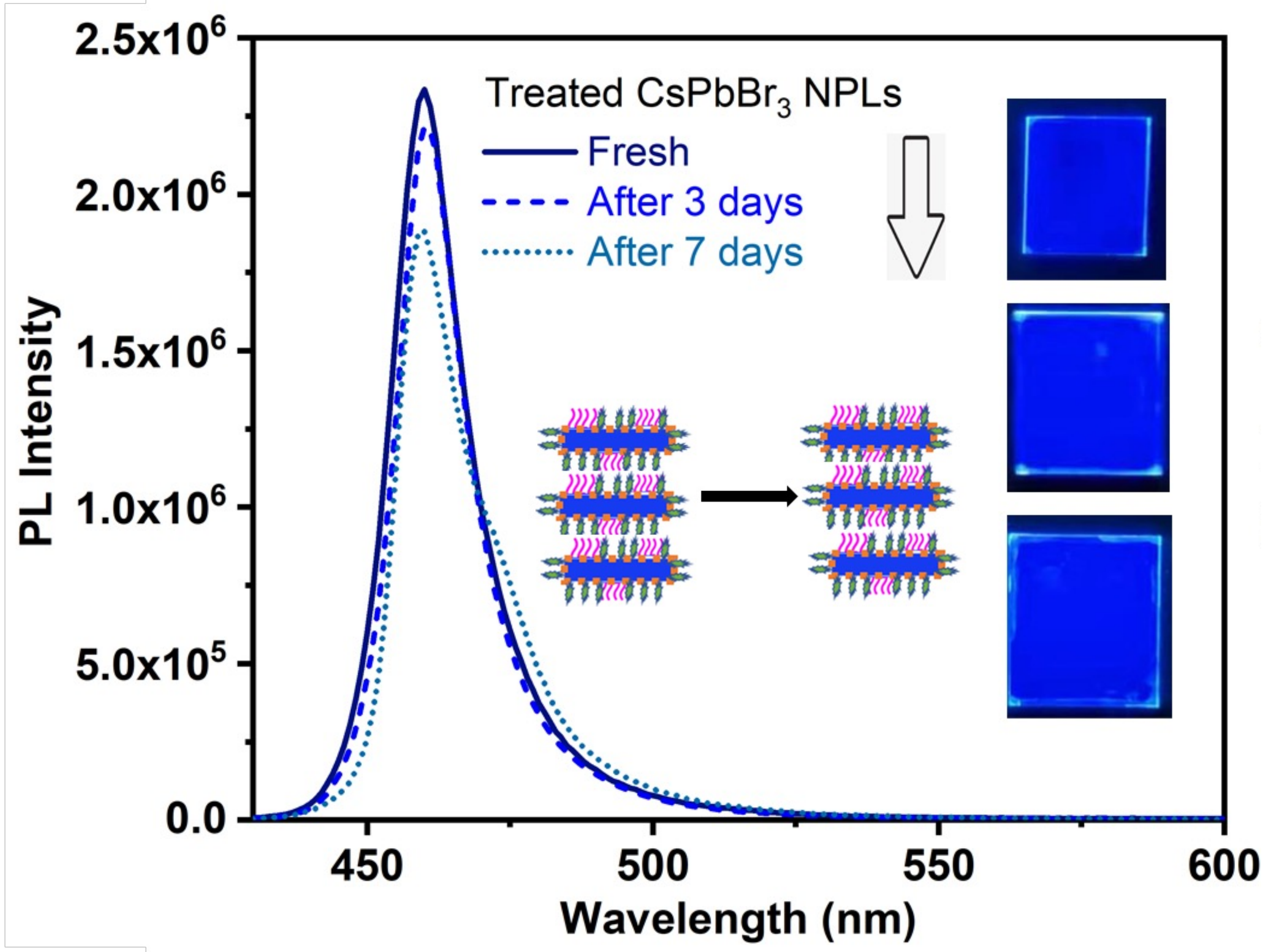




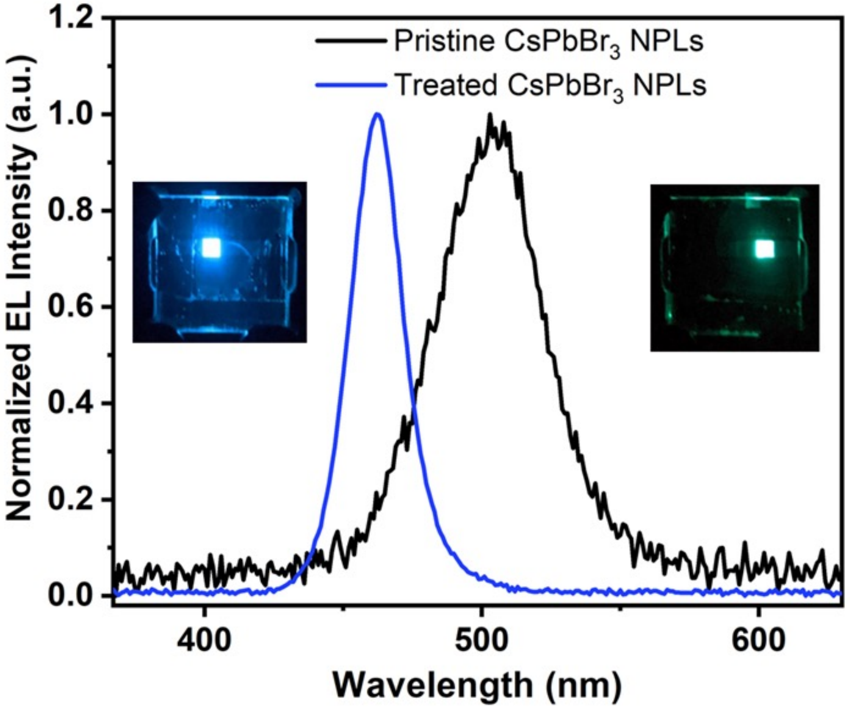
Sample	PLQE (%)	Lifetime (ns)
Pristine $CsPbBr_3$	28	1.85
Treated $CsPbBr_3$	85	12.5

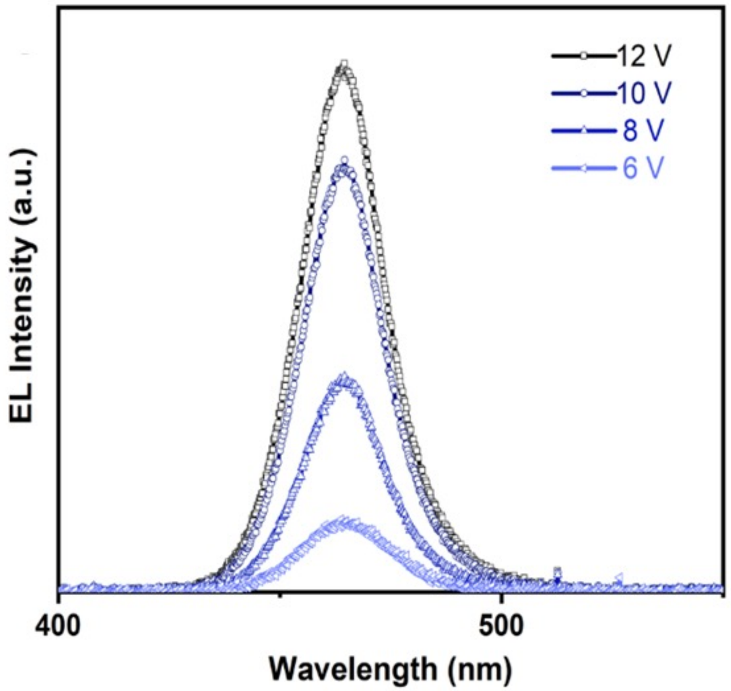
Enhanced Stability

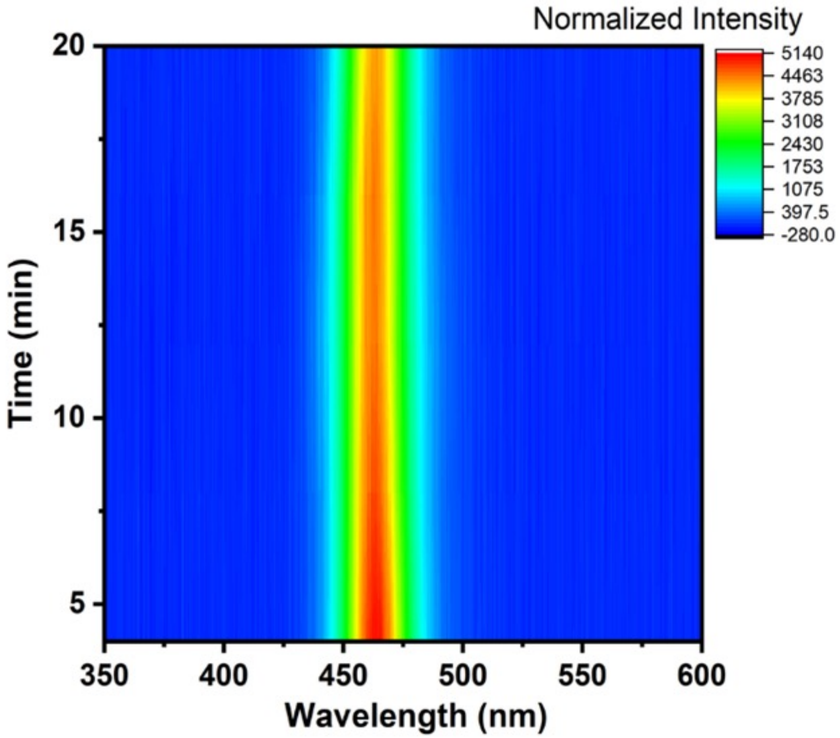




Device Performance



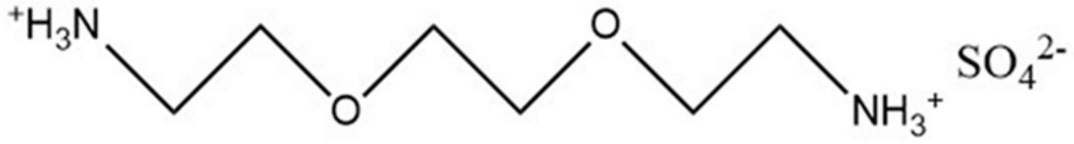




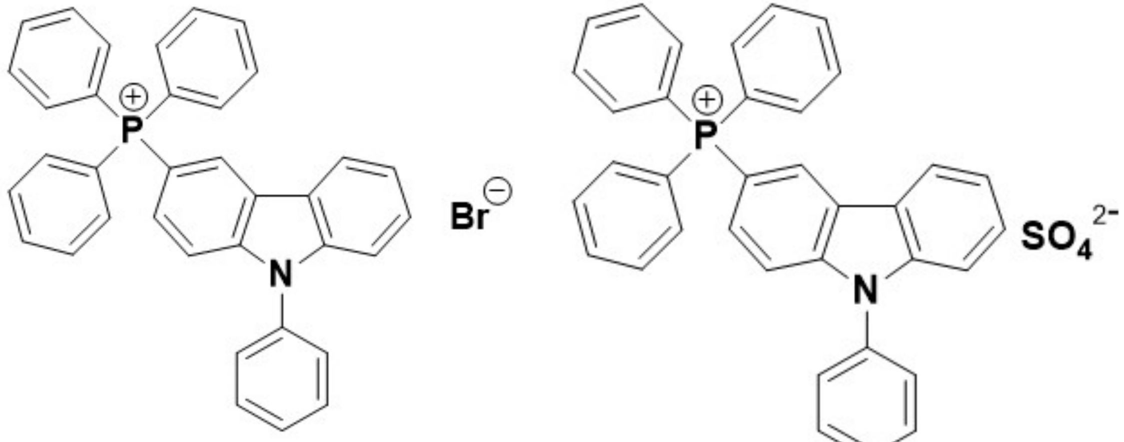
- $DBESO_4$ ligand prevents the aggregation and degradation of $CsPbBr_3$ NPLs.
- Blue PeLEDs based on treated $CsPbBr_3$ NPLs showed blue emission at 462 nm with excellent spectral stability.
- The devices showed external quantum efficiencies (EQE) of up to 1.77% with a peak luminance of 691 cd m^{-2}.
- The half lifetime (T50) at an initial luminance of 100 cd m^{-2} for an un-encapsulated device is 20 minute.

Advanced Energy Materials, **2023**, *13*, 2201605

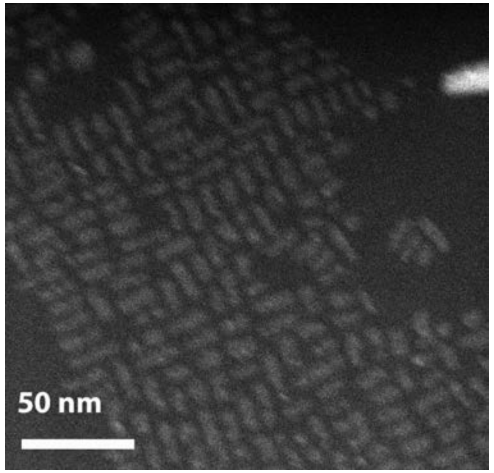
Changing Surface Passivating Ligands

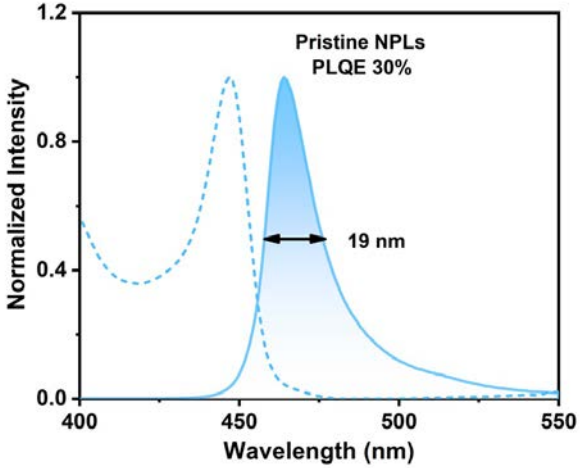


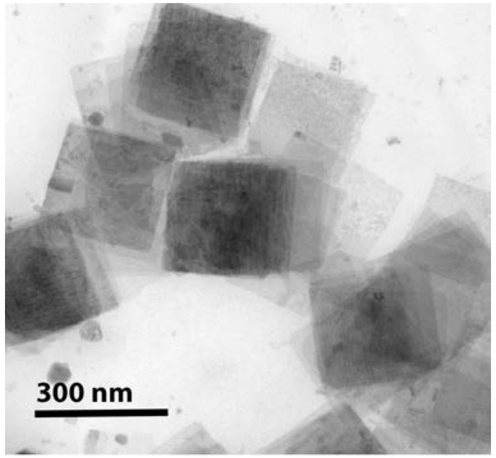
Isolating organic salt, $EDBESO_4$

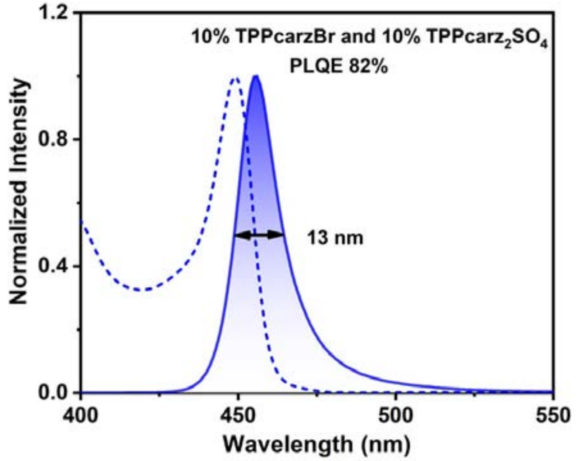


Semiconducting organic salts, TPPcarzBr and $TPPcarz_2SO_4$

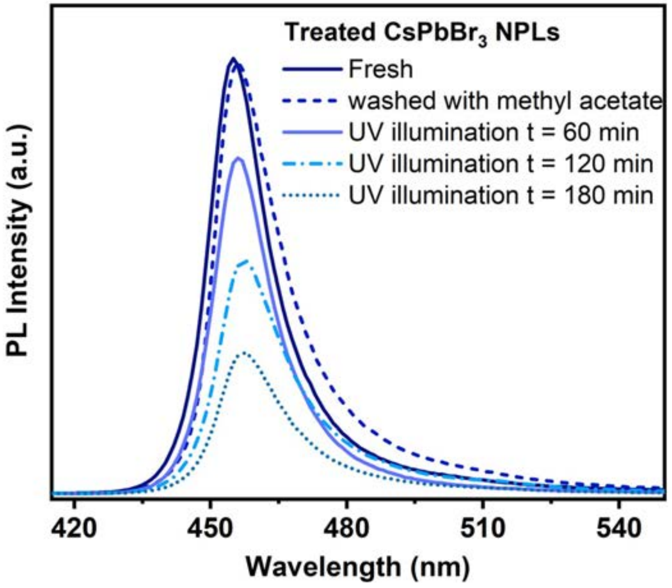


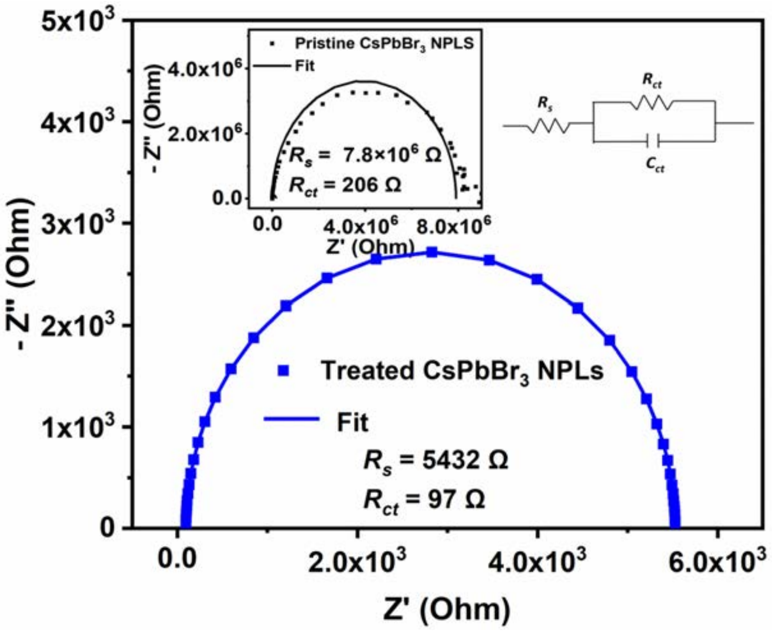


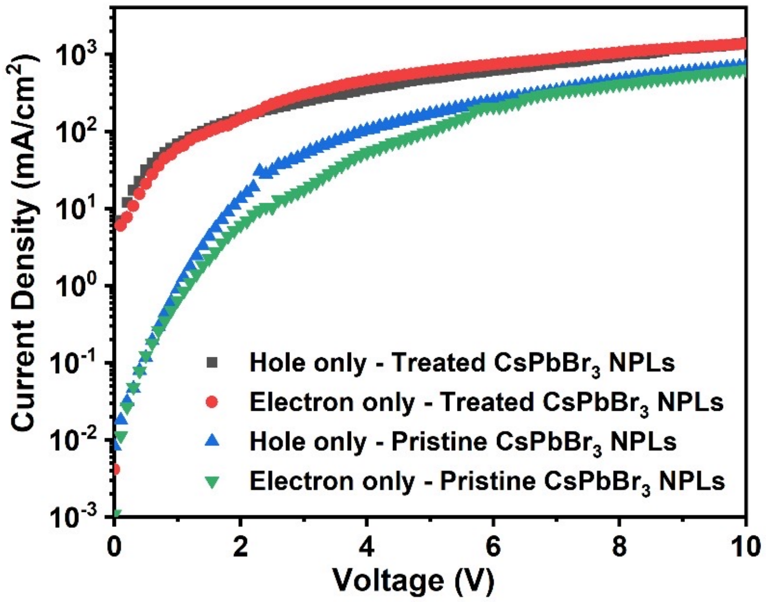


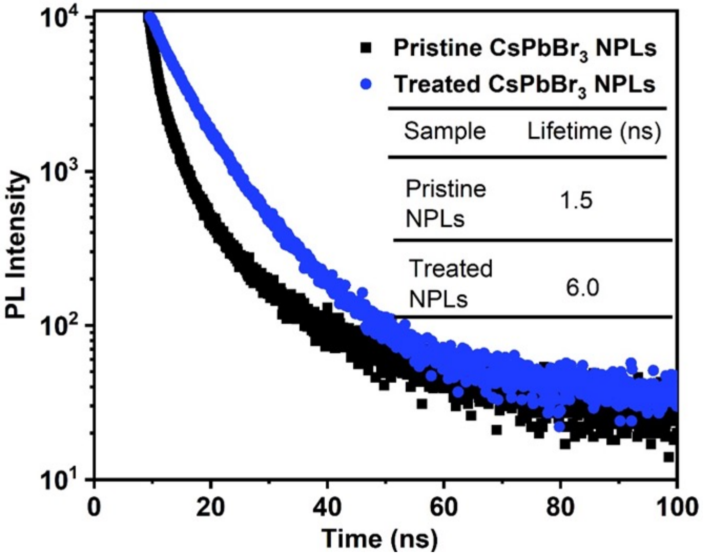


Enhanced Properties





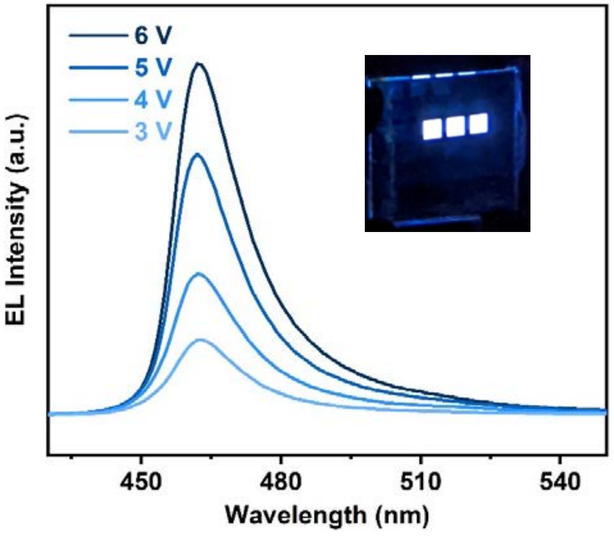


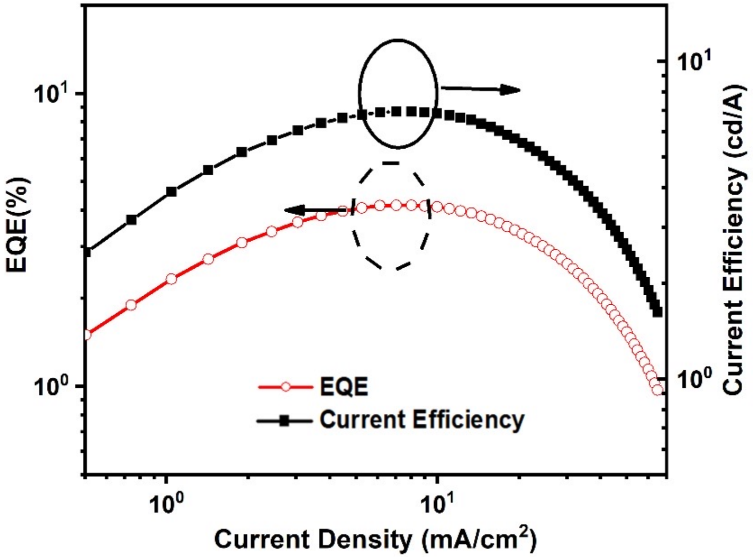


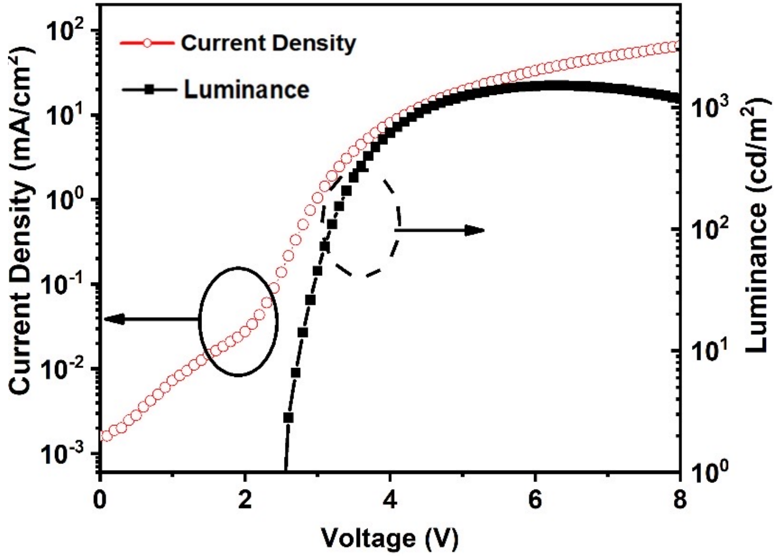
- SO_4^{2-} can bind uncoordinated Pb^{2+} to passivate the surface defects and suppress the coalescence of $CsPbBr_3$ NPLs.
- The presence of Br^- from TPPcarzBr could reduce Br^- vacancies on $CsPbBr_3$ NPLs, resulting in enhanced PLQEs.
- Partially replacing long alkyl chain insulating ligands with organic semiconducting ligands for the surface passivation of $CsPbBr_3$ NPLs improves the electronic properties.

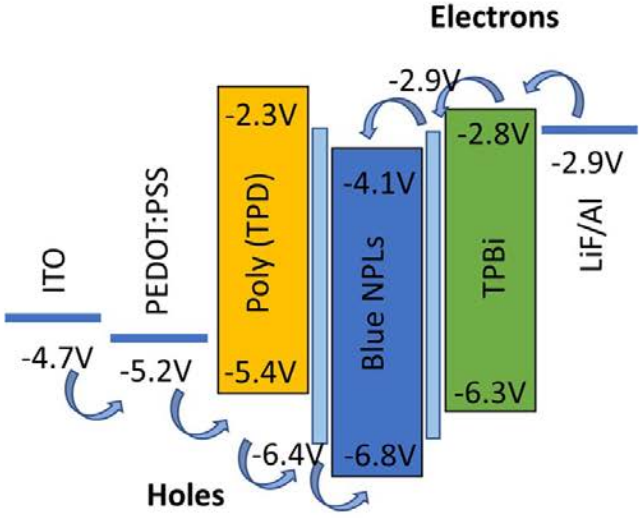
MA•GROUP
Advanced Materials for Electronics & Energy Devices

Device Performance









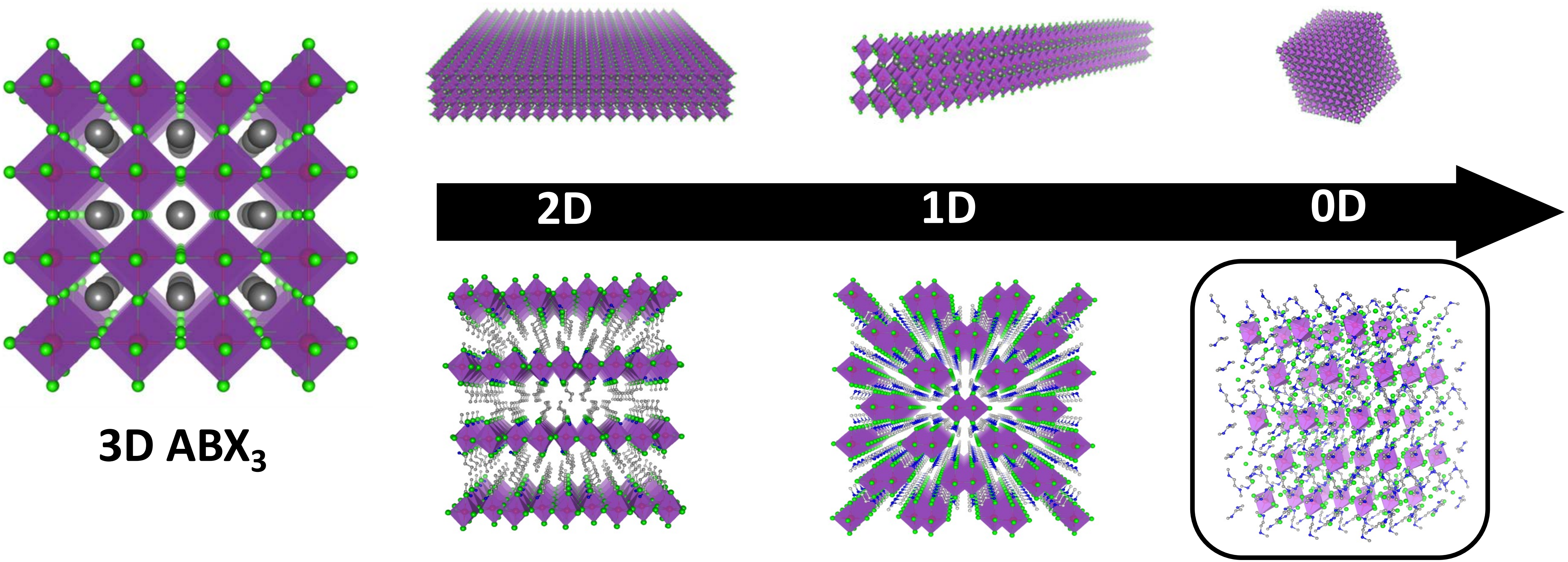
Emitting Layer	EL peak (nm)	Luminance (cd/m^2)	EQE (%)	Half lifetime (T_{50}) (min)
Pristine $CsPbBr_3$ NPLs	**501**	**234**	**0.24**	**0.5**
Treated $CsPbBr_3$ NPLs	**455**	**1511**	**4.15**	**50**

ACS Energy Letters **2023**, *8*, 4259–4266

MA·GROUP
Advanced Materials for Electronics & Energy Devices

Beyond Halide Perovskites

➢ **Morphological Low Dimensional Metal Halide Perovskites (Still ABX_3)**

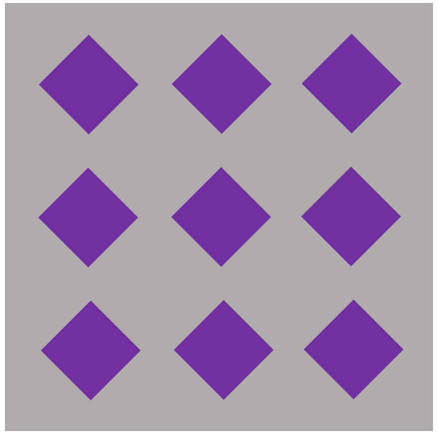


➢ **Molecular Level Low Dimensional Organic Metal Halide Hybrids**

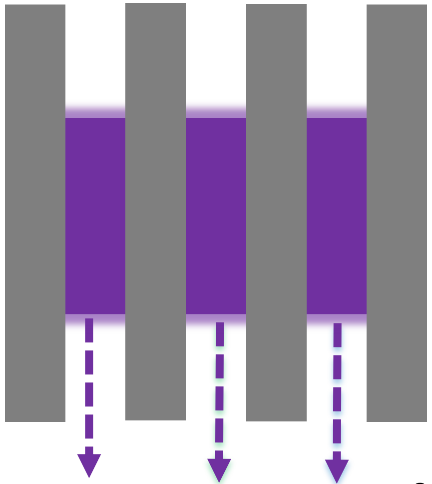
ACS Energy Letters, **2018**, *3*, 54-62; *Materials Research Letters*, **2018**, *6*, 552-569; *Materials Science & Engineering - R: Reports*, **2019**, *137*, 38-65; *Advanced Optical Materials*, **2021**, *9*, 2001766

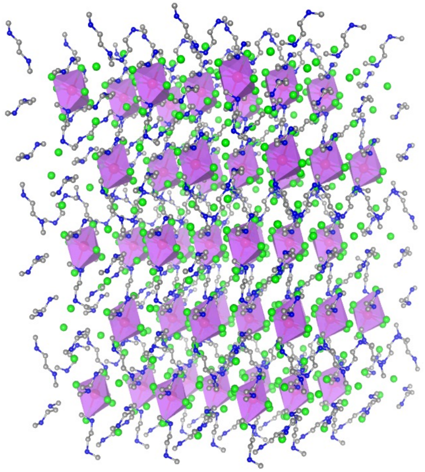
MA·GROUP
Advanced Materials for Electronics & Energy Devices

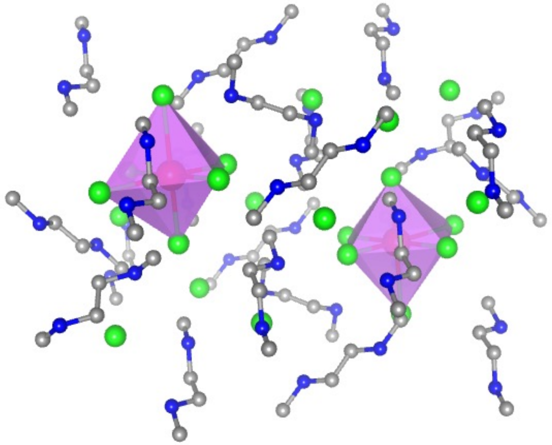
0D Organic Metal Halide Hybrids

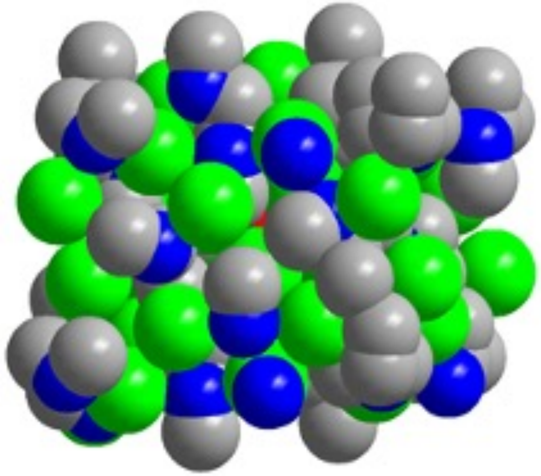


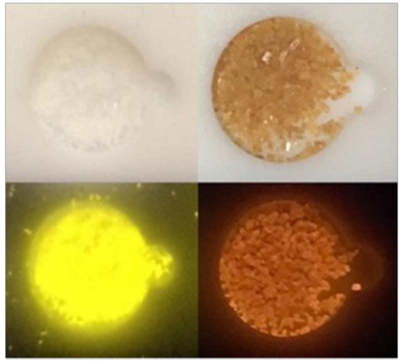
Perfect Host-Dopant System

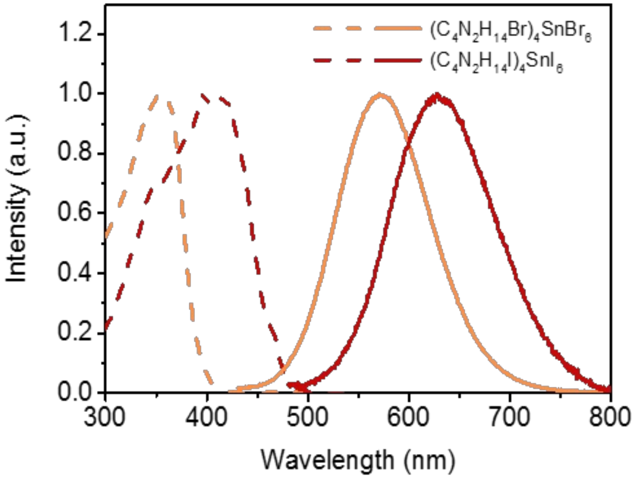


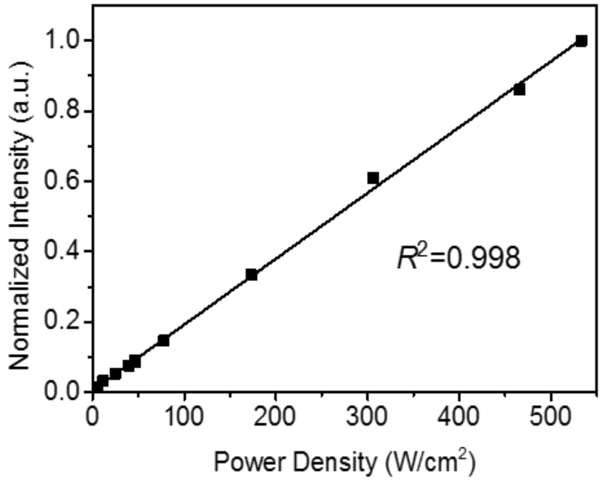








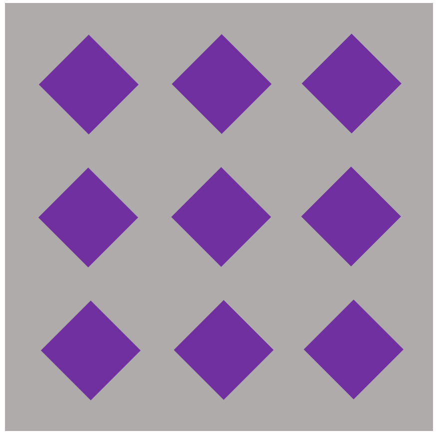




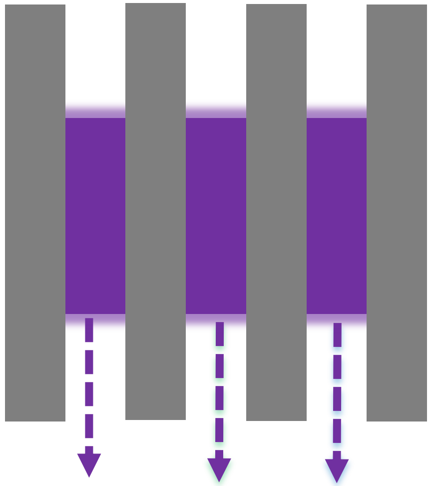
Luminescent 0D Sn halide hybrids with near-unity PLQE!

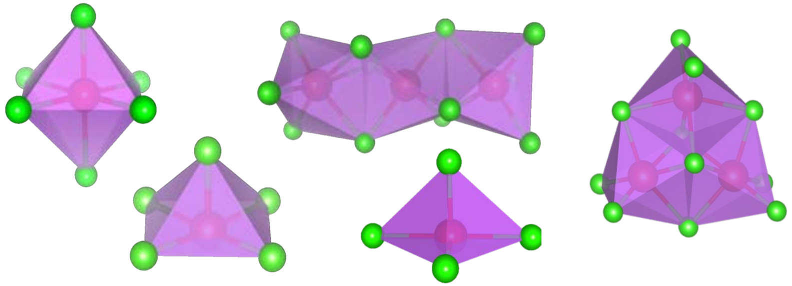
Angewandte Chemie International Edition, **2017**, 56, 9018-9022; *Chemical Science*, **2018**, *9*, 586-593

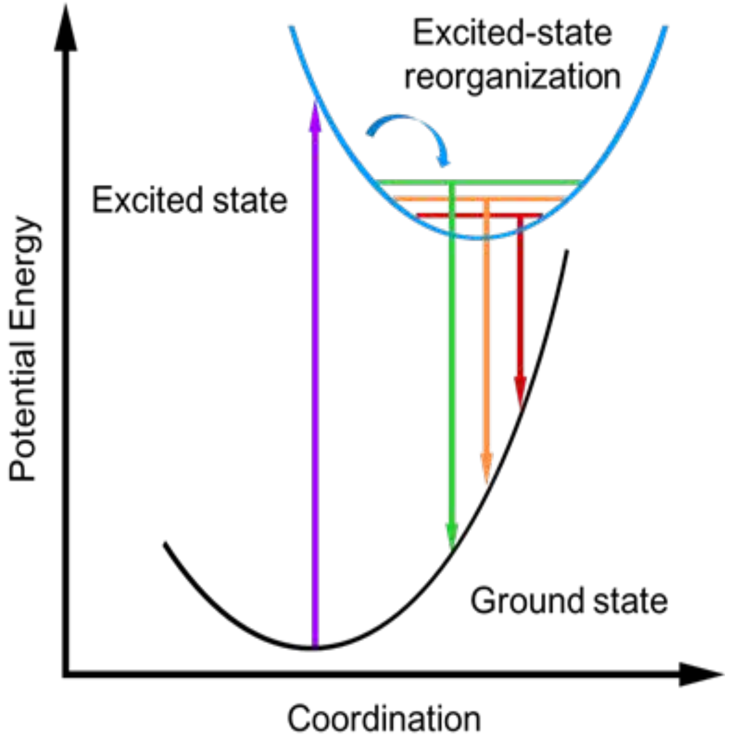
0D Organic Metal Halide Hybrids

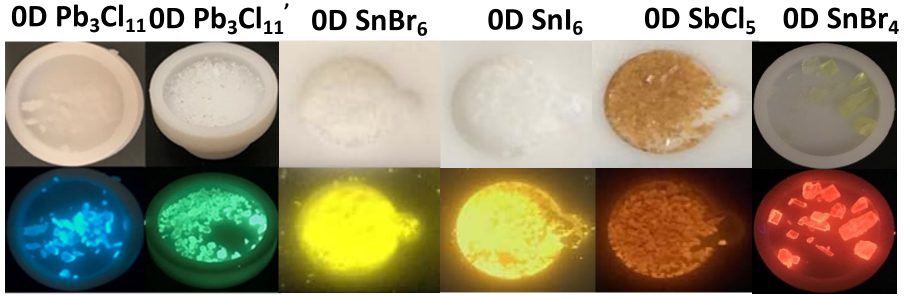


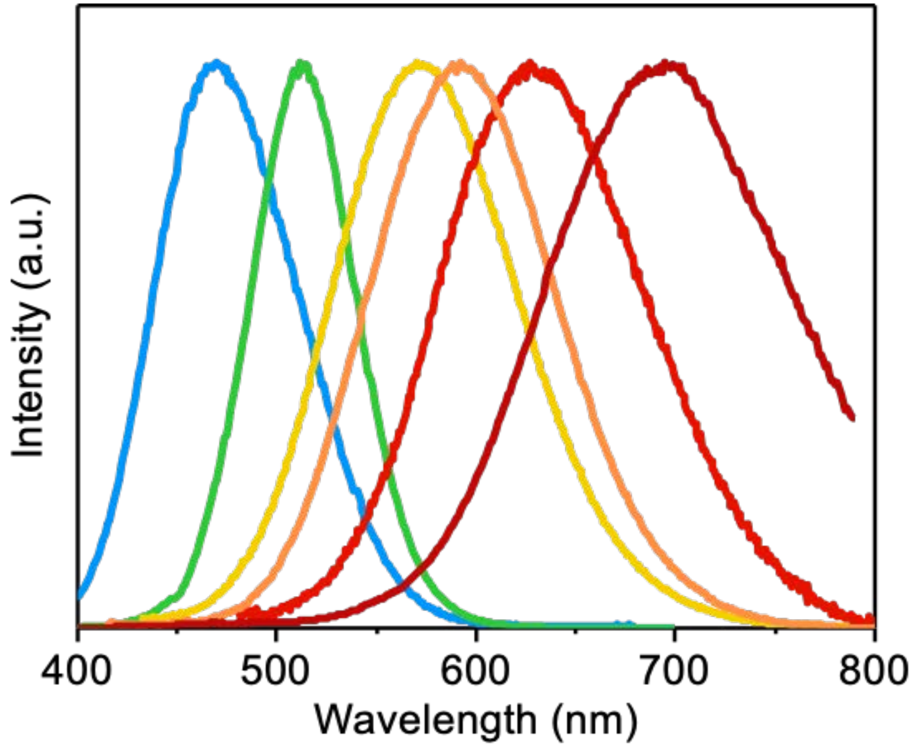
Perfect Host-Guest System





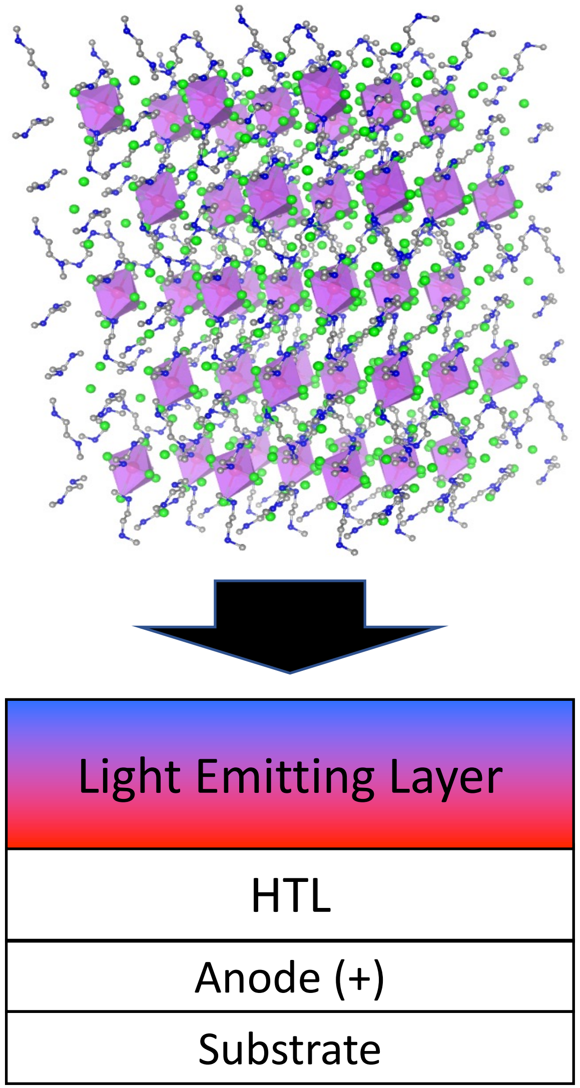


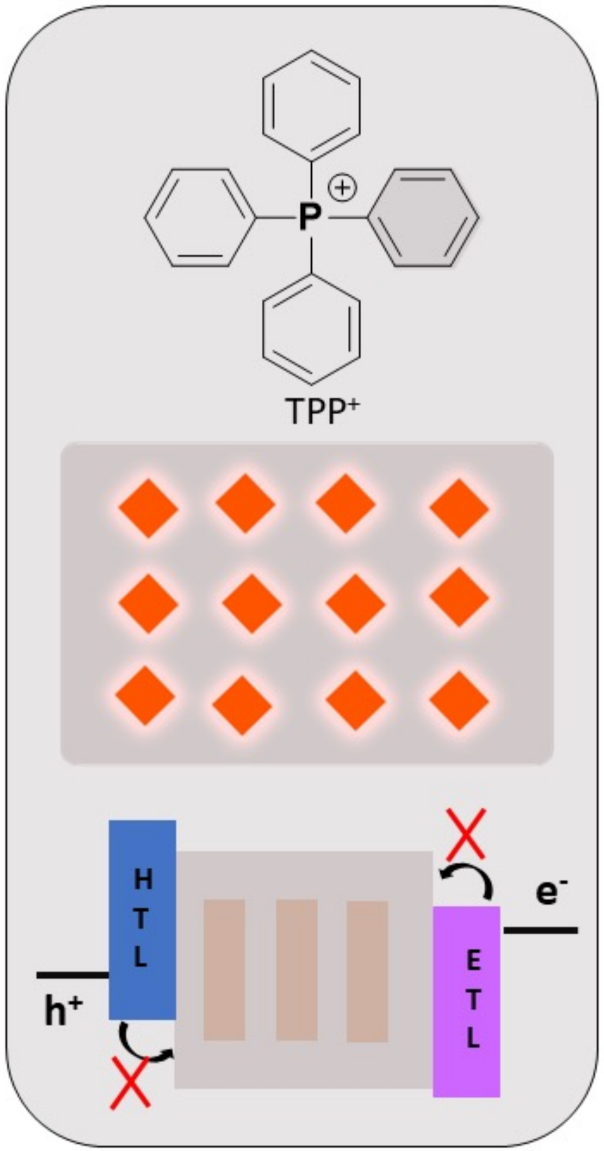


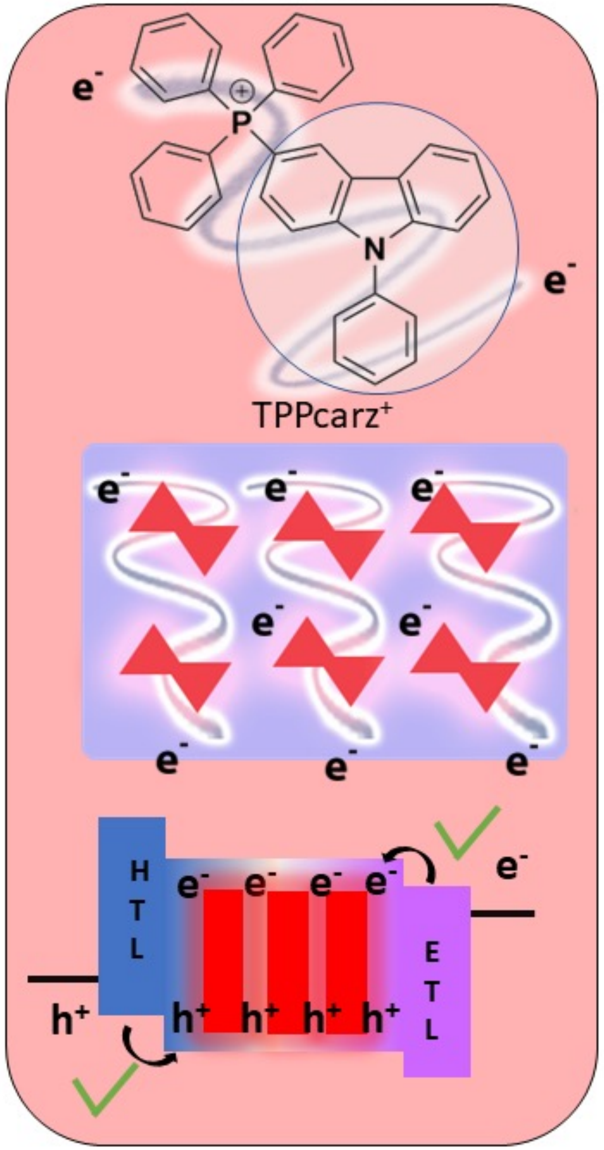


Chemical Science, **2018,** 9, 586-593; *JACS*, **2018**, *140*, 13181-13184; *Angew. Chem. Int. Ed.*, **2017**, 56, 9018-9022; **2018**, 57, 1021-1024; **2020**, *59*, 14120-14123; *ACS Energy Letters*, **2018**, *3*, *54-62;* **2018**, *3*, 1443-1449; **2019**, *4*, 1579-1583; *ACS Materials Letters*,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

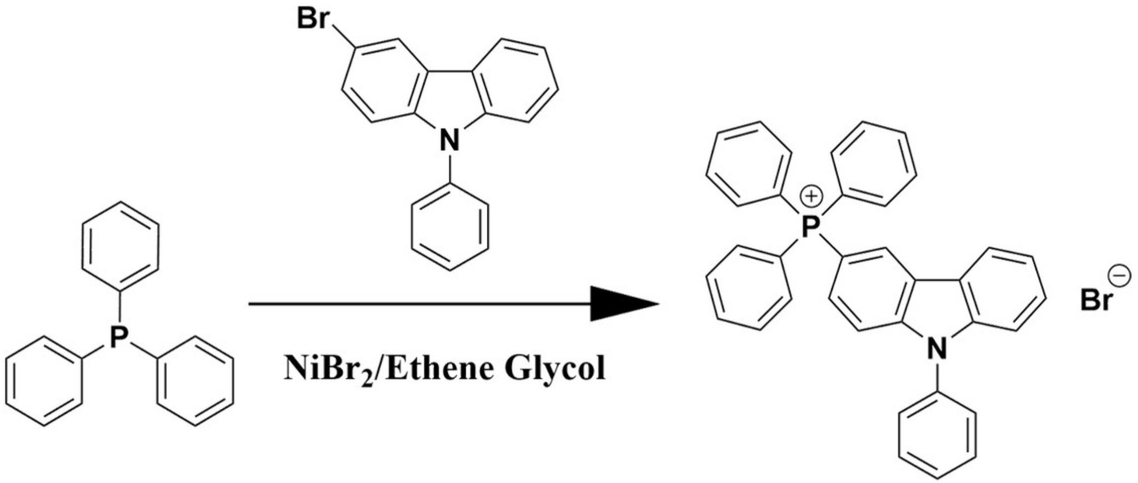
To Achieve Electroluminescence

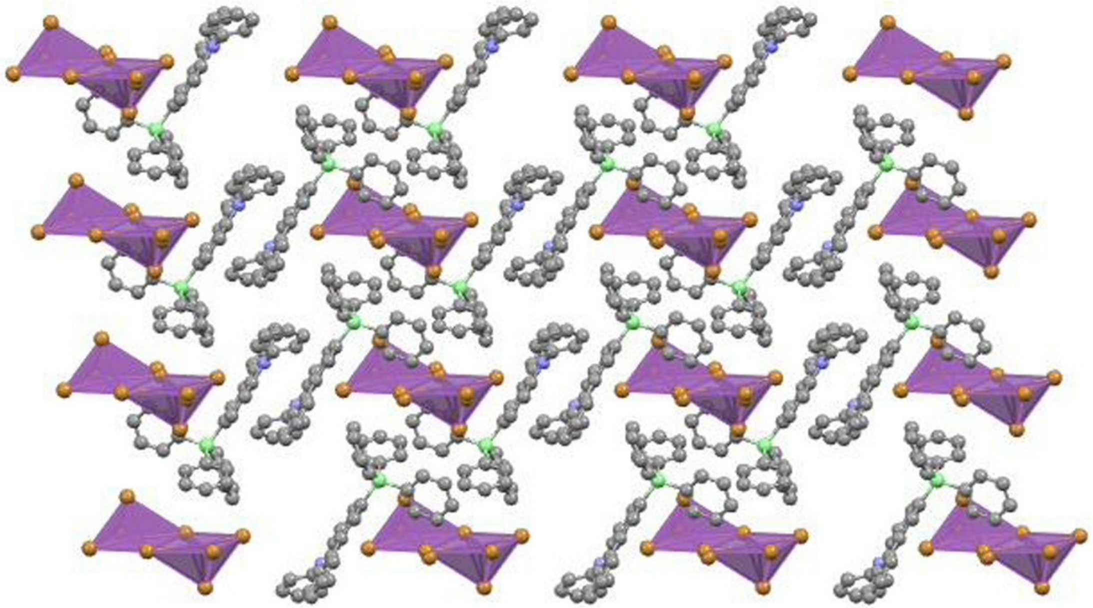


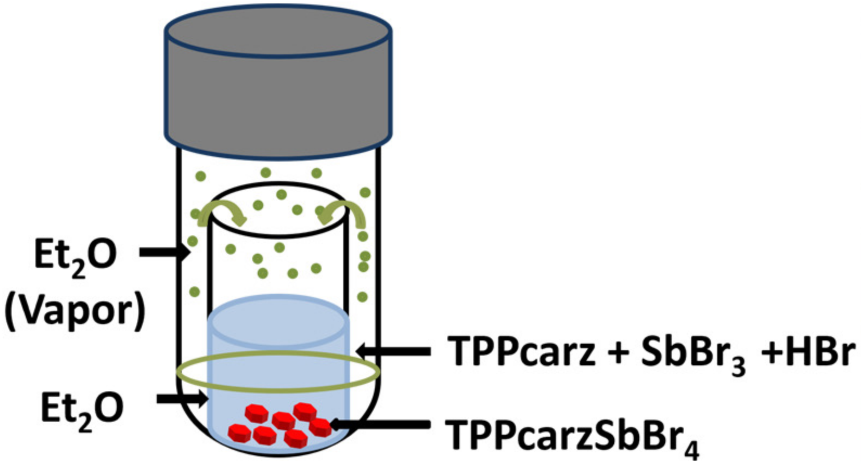


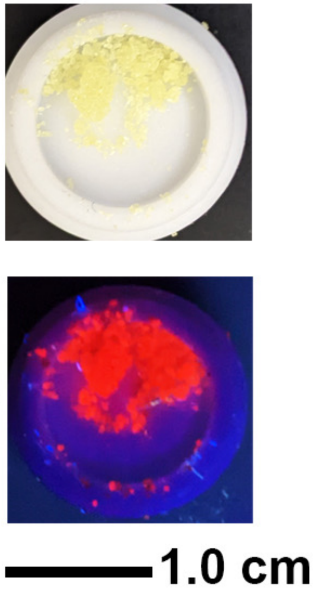


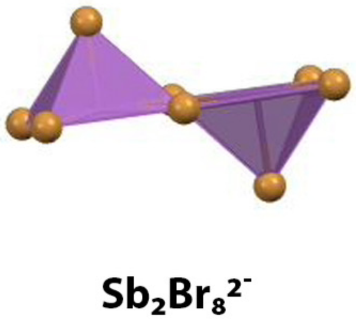
0D Containing Organic Conductors

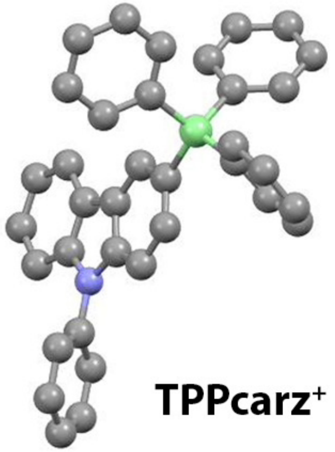




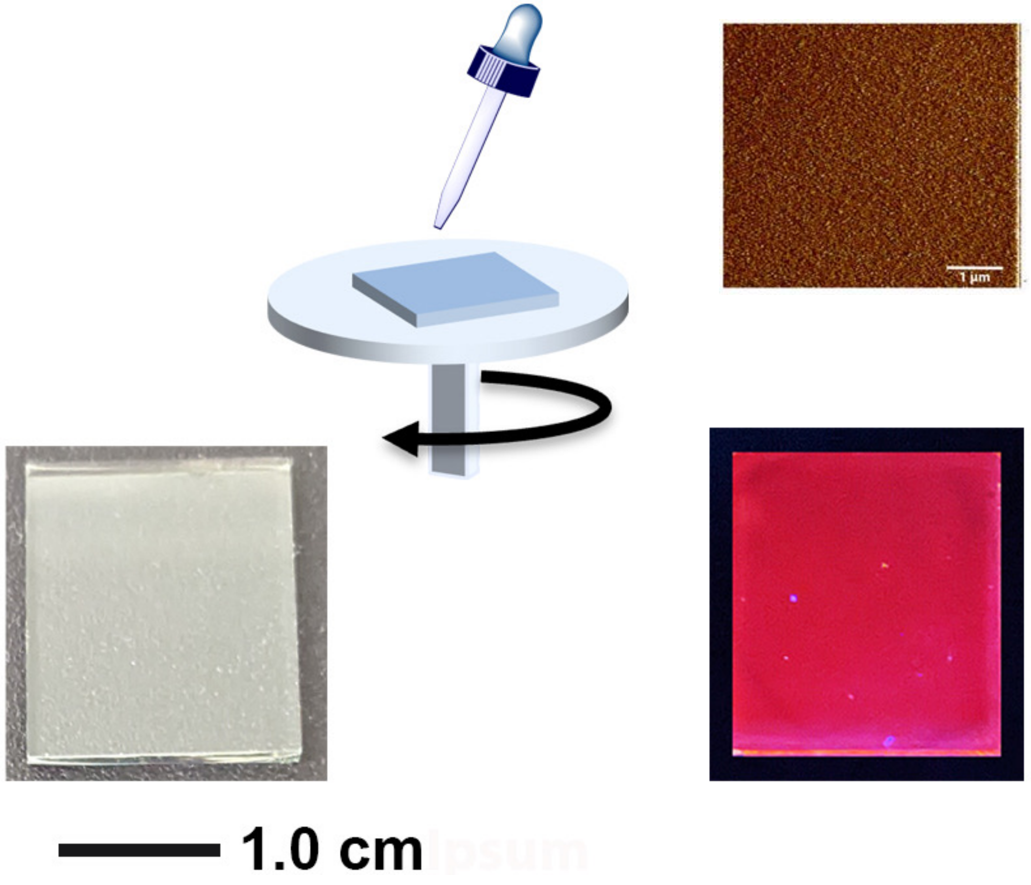


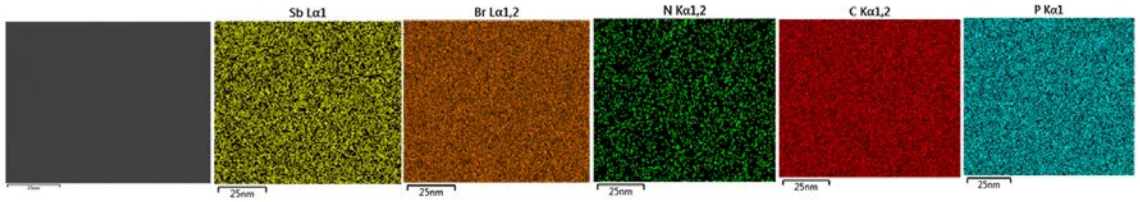


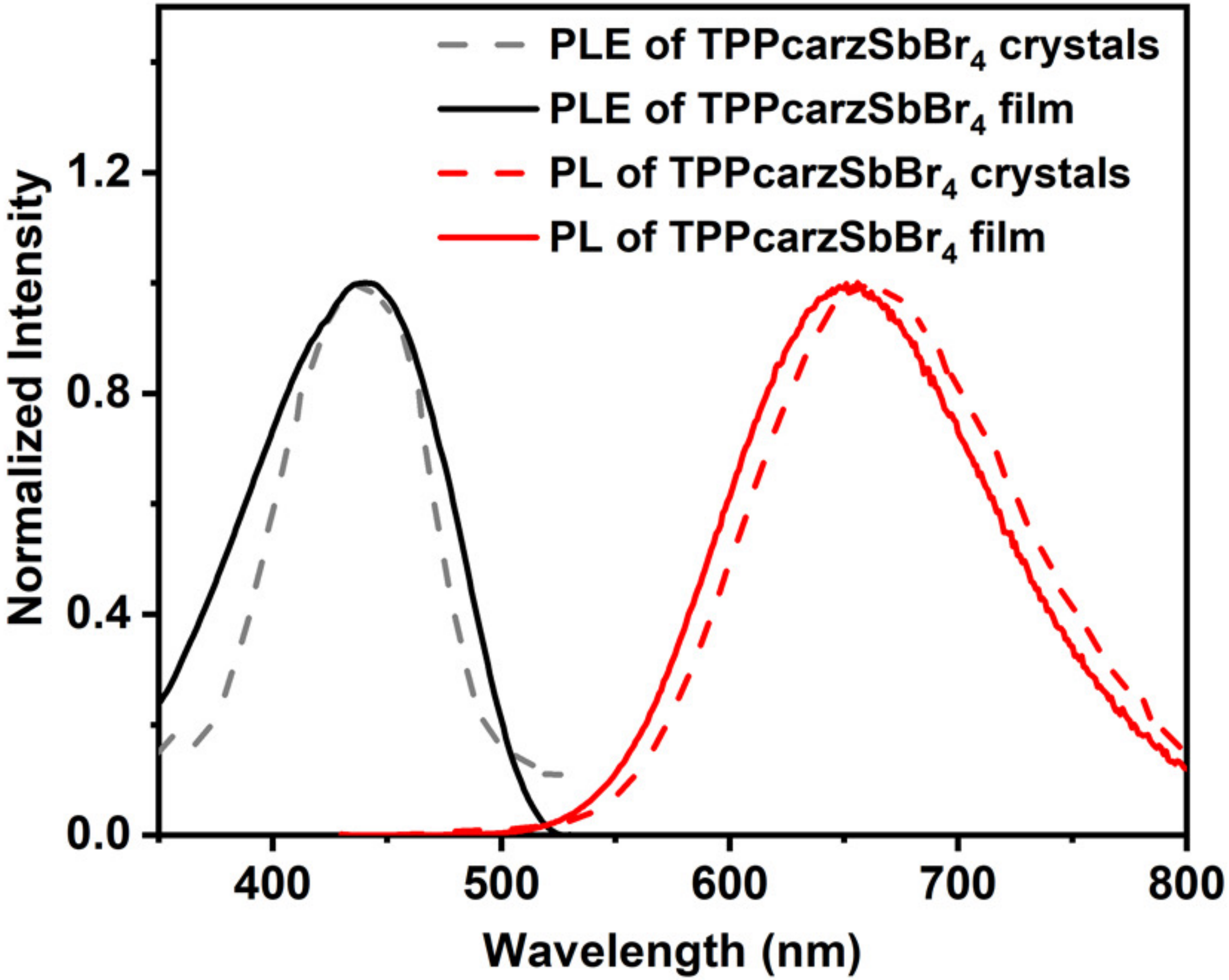




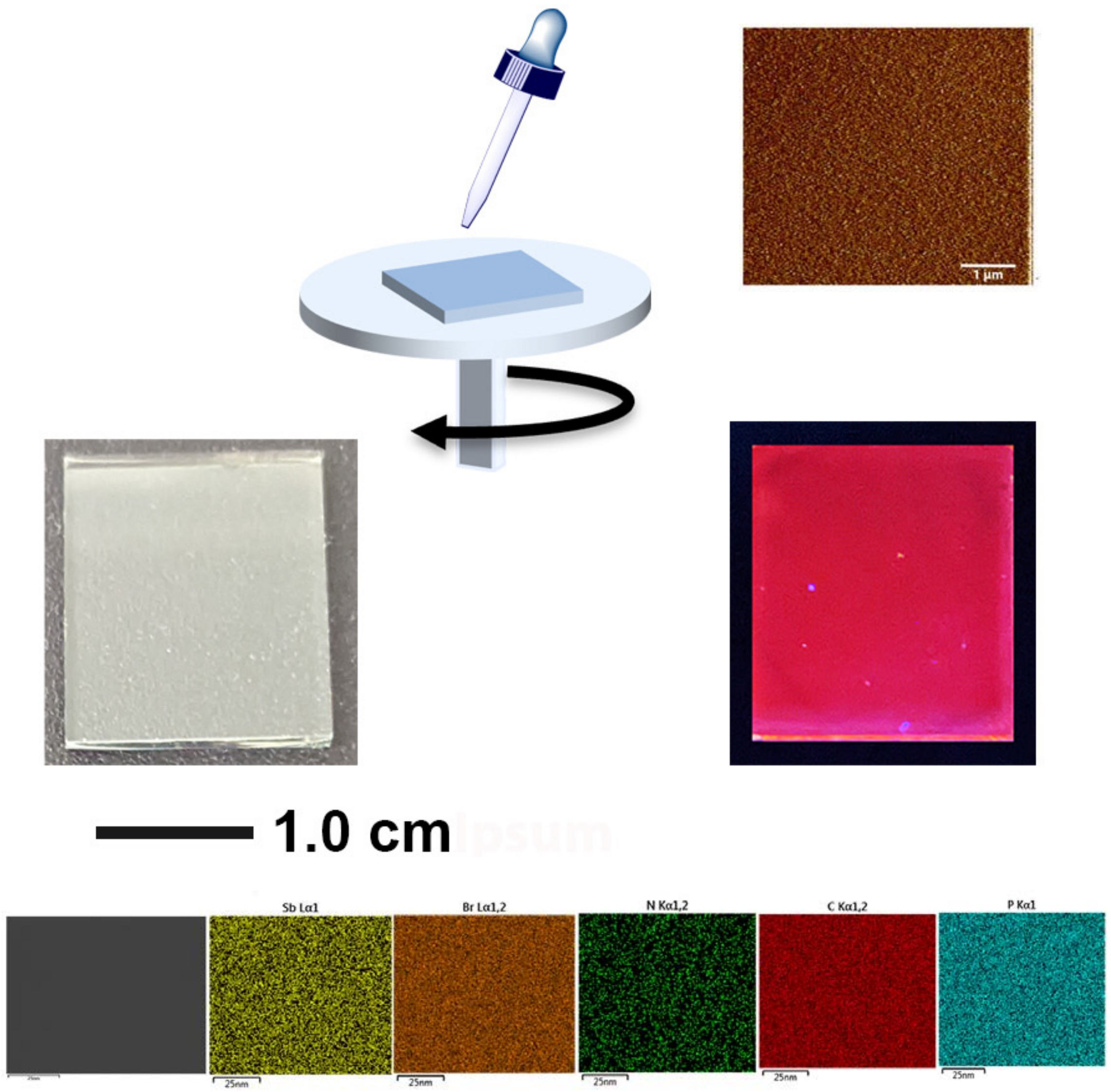
Solution Processed Thin Films

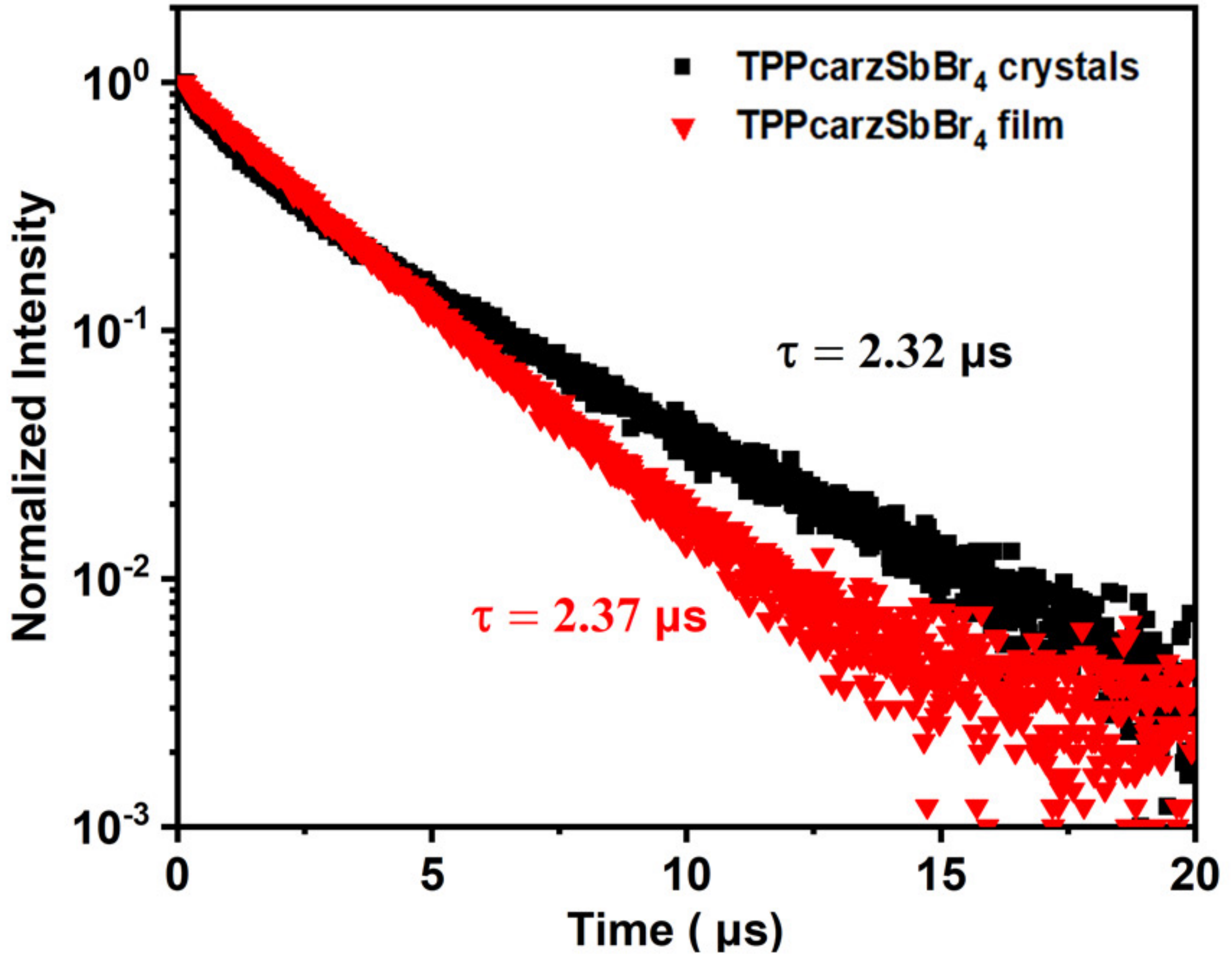




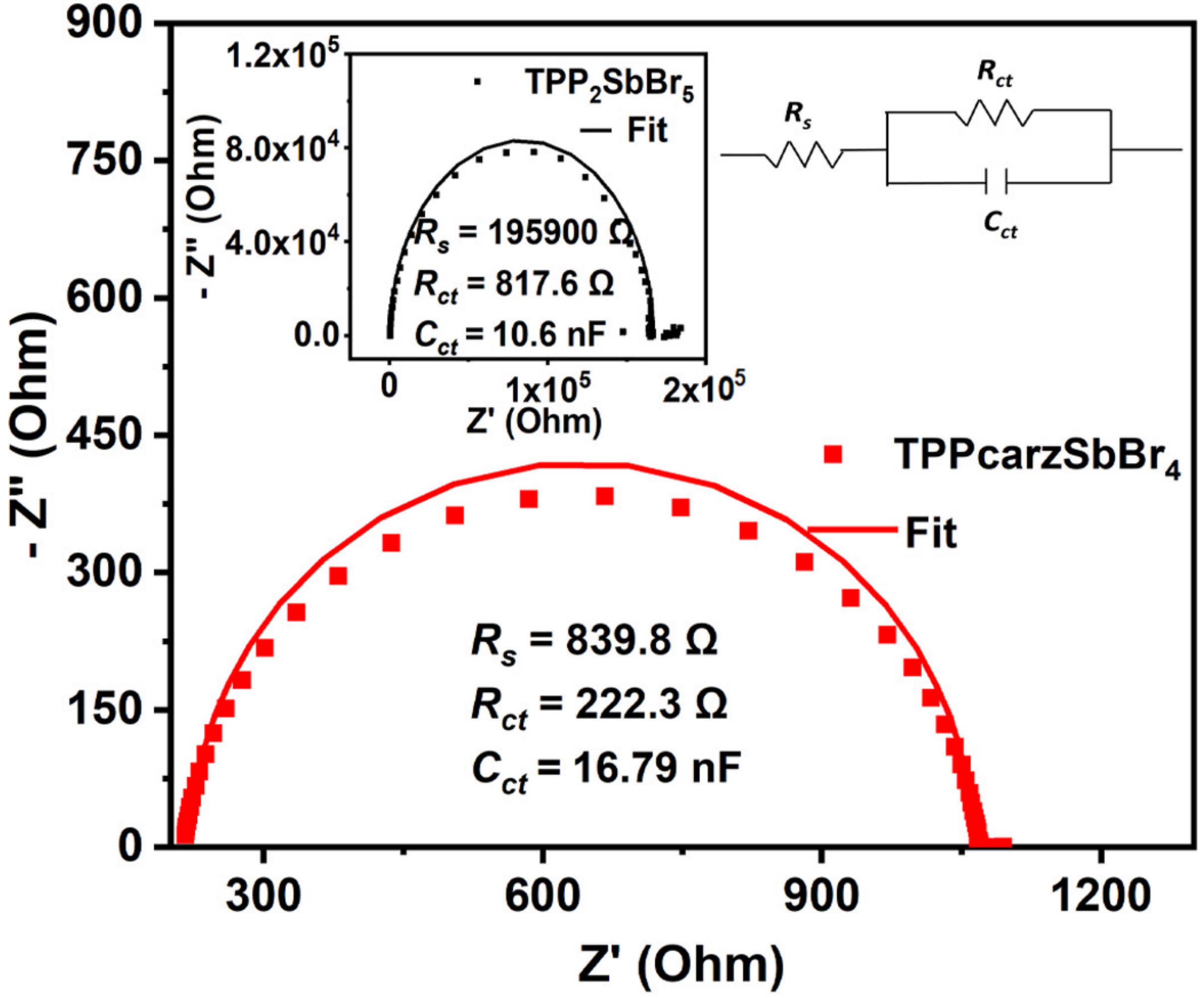


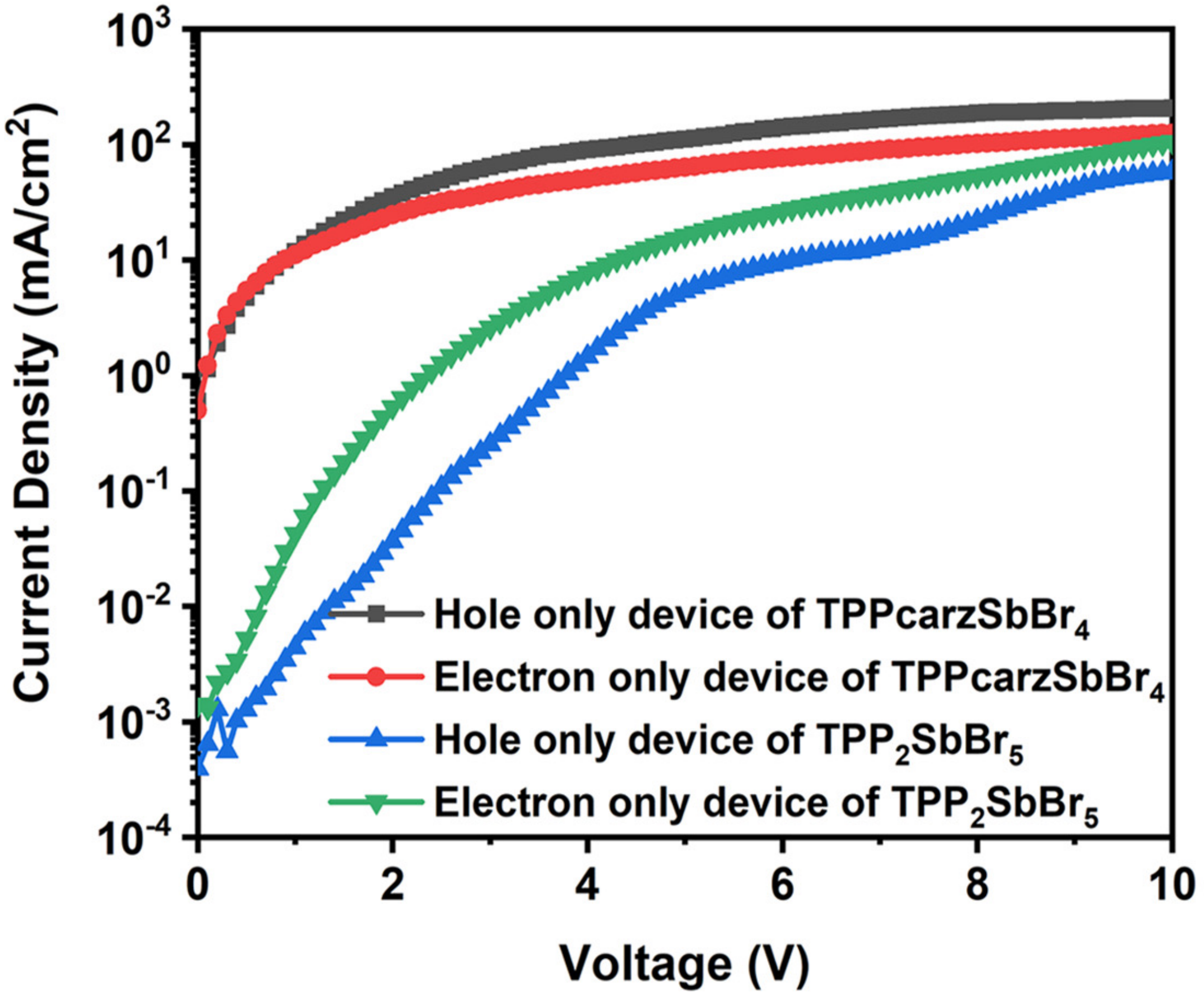
Solution Processed Thin Films





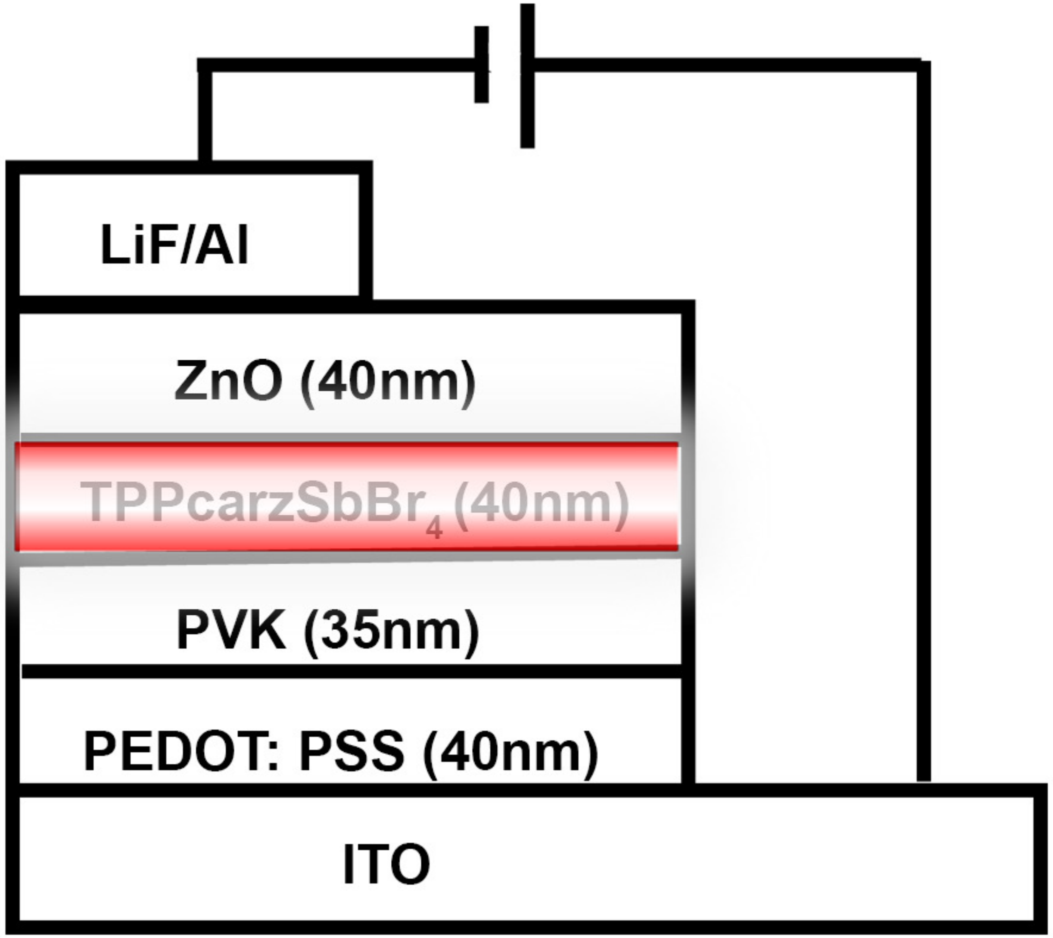
Enhanced Electronic Properties

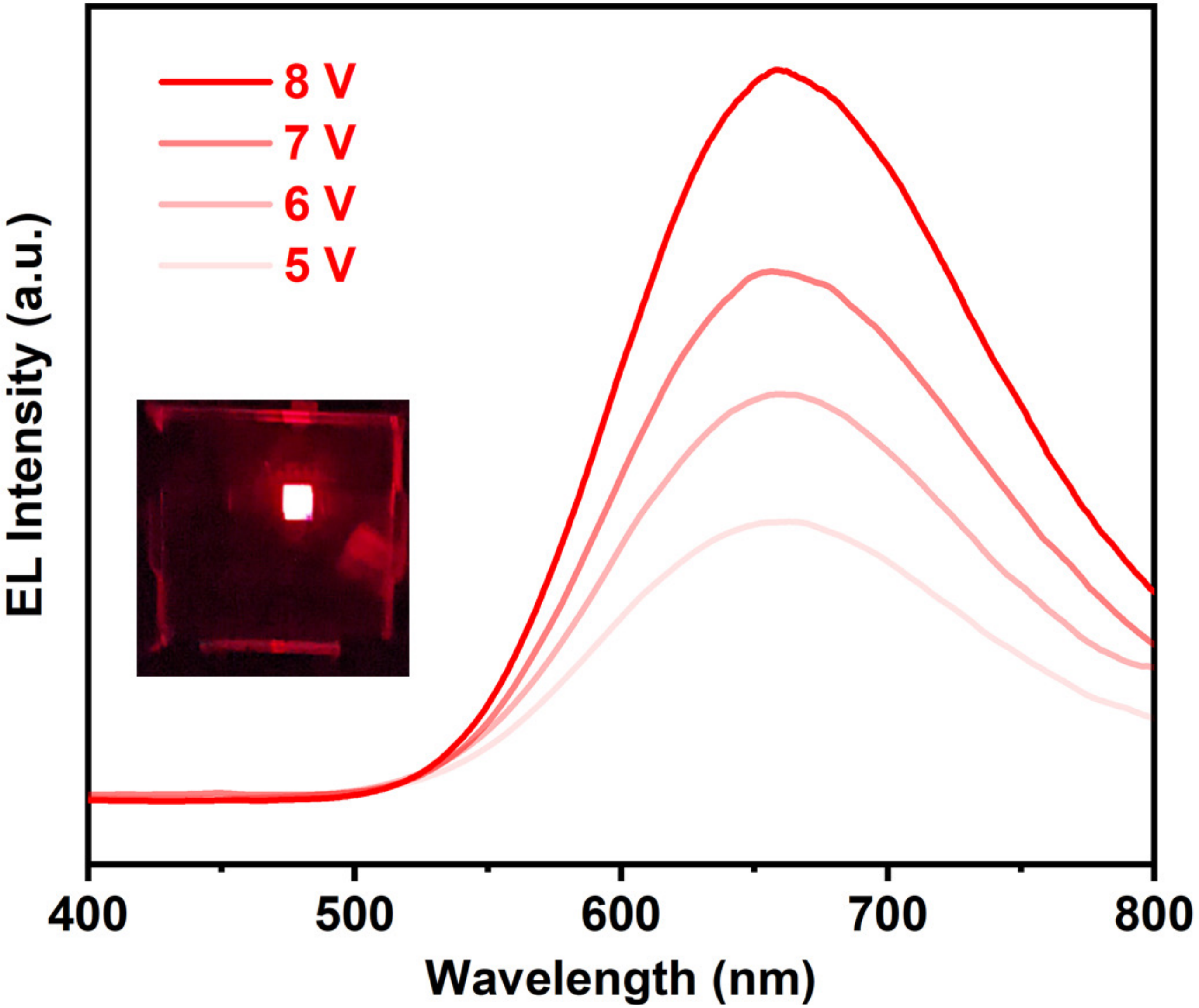




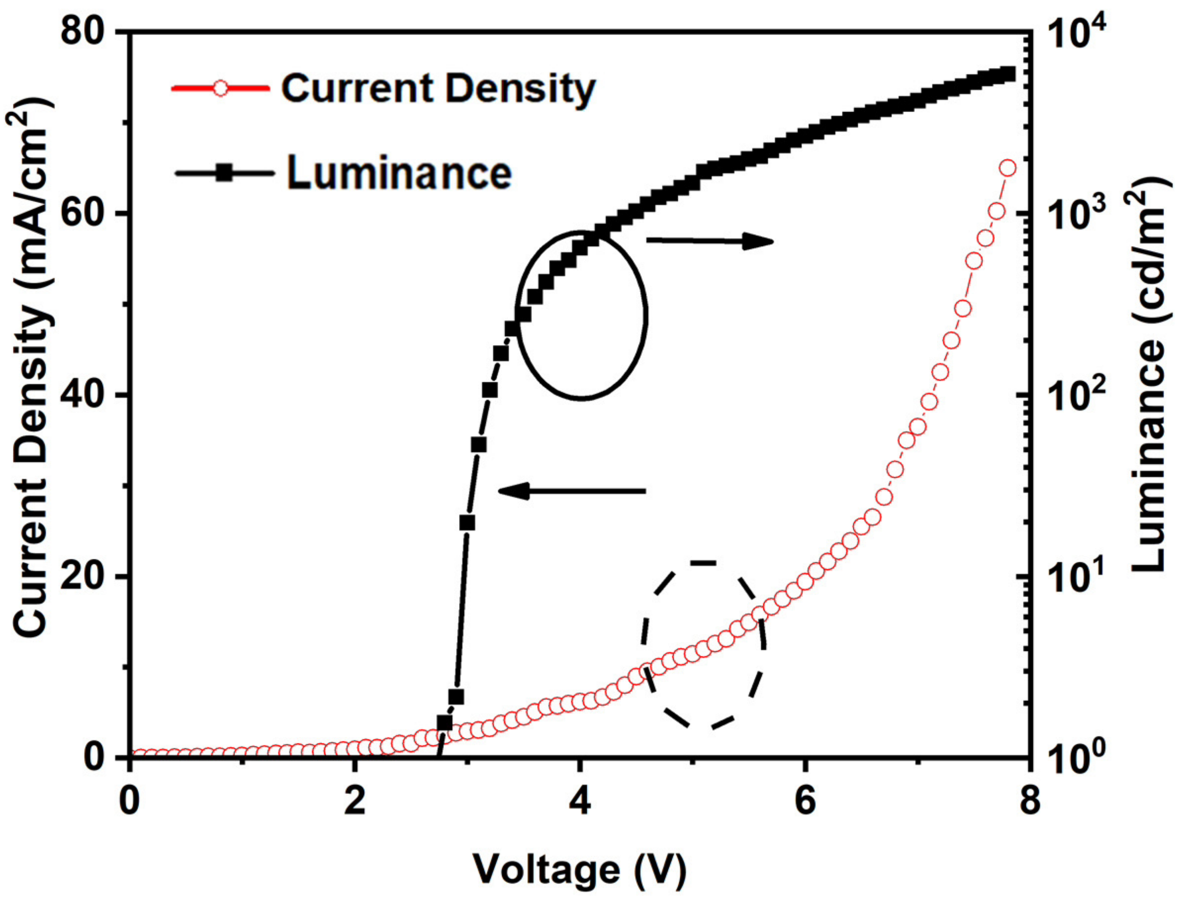
MA•GROUP
Advanced Materials for Electronics & Energy Devices

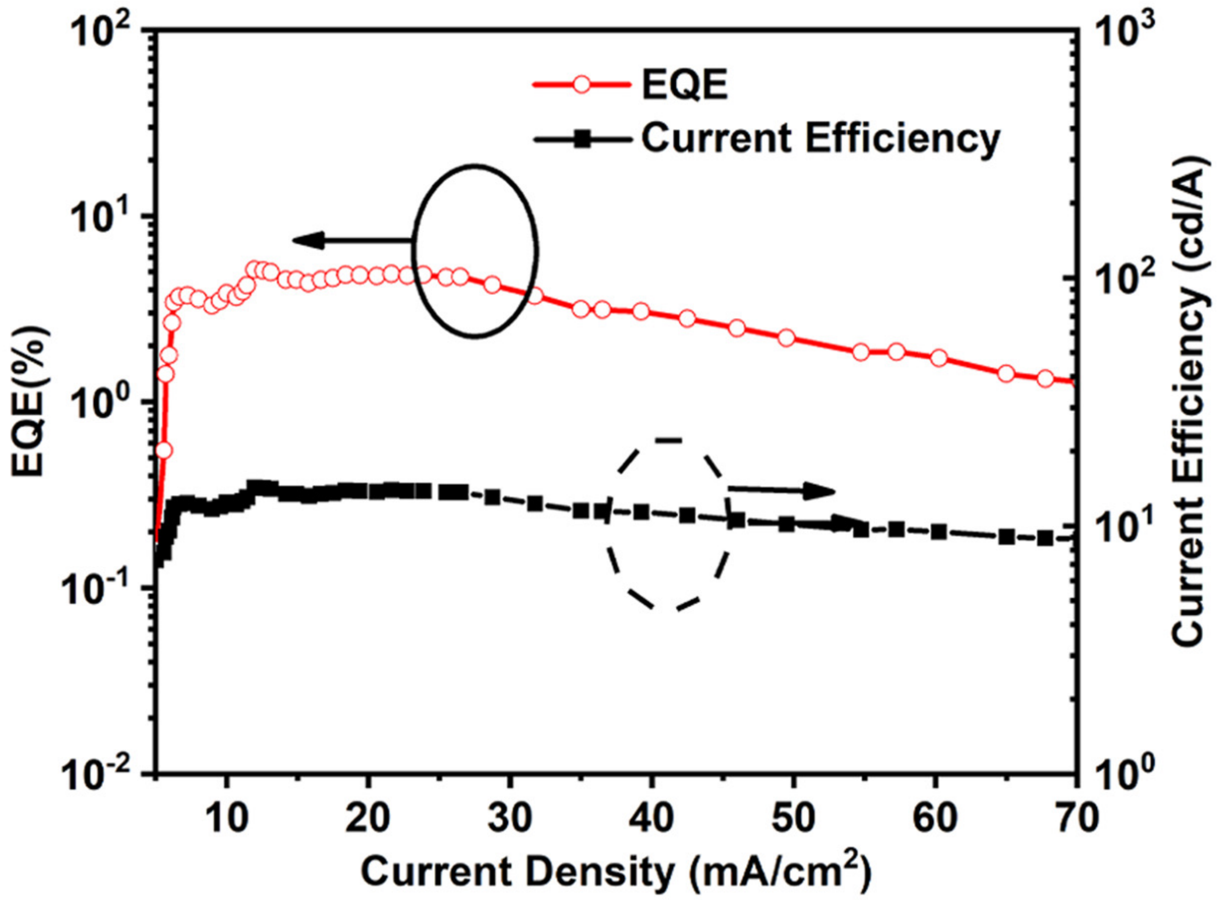
Electroluminescent Devices





Electroluminescent Devices



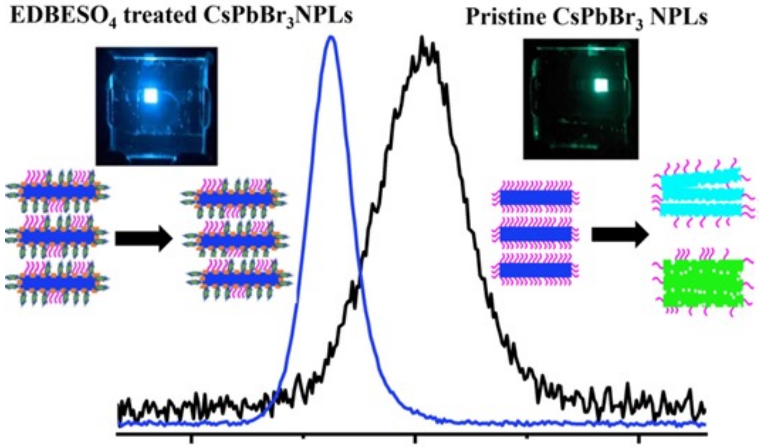


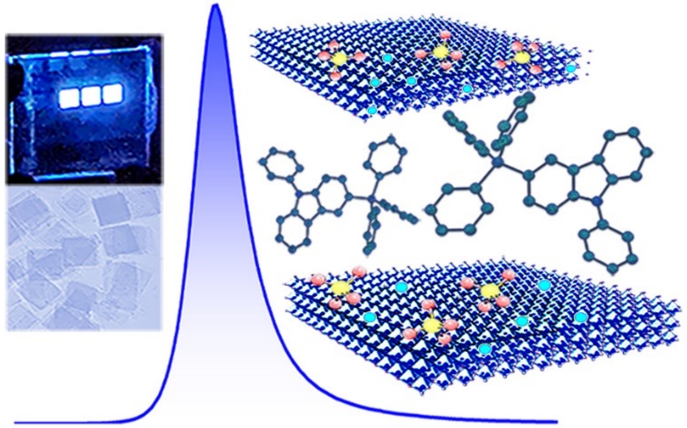
LEDs based on a 0D organic metal halide hybrid exhibit an EQE of 5.12%, a peak luminance of 5957 cd m^{-2}, and a current efficiency of 14.2 cd A^{-1}.

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

Conclusions

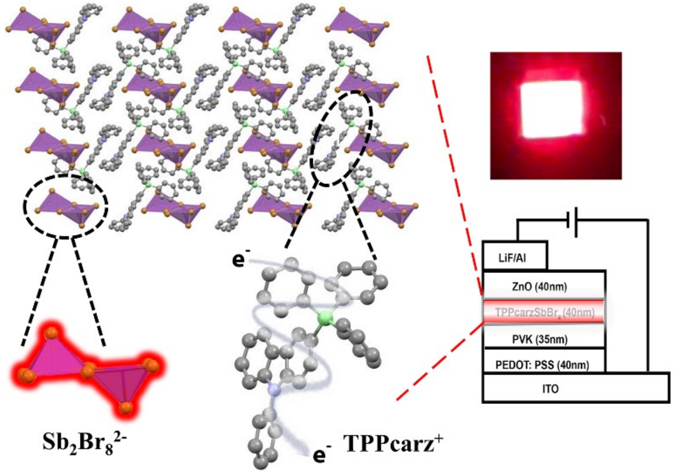
- **Blue emitter**





Improving the stability and charge transport of blue perovskite NPLs for LEDs

- **Red emitter**



Designing 0D organic metal halide hybrids containing semiconducting organic cations for LEDs

Advanced Energy Materials, **2023**, *13*, 2201605; *ACS Energy Letters* **2023**, *8*, 4259–4266; *Advanced Materials* **2023**, *35*, 2209417

Take Home Messages

- LEDs based on metal halide perovskites and perovskite related materials are highly promising, but numerous issues and challenges need to be addressed before their commercialization.
- With the realization of efficient color pure green and red PeLEDs, the development of comparably efficient blue PeLEDs is necessary for applications in full-color displays.
- Inspired by the advances of QDLEDs, developing inorganic core-shell PeQDs has the potential to be the solution to many of PeLEDs' ailments.
- For lead-free PeLEDs, many perovskite-related metal halide materials could offer alternative routes to efficient and stable LEDs.
- With the advent of new display industries, the narrow emissions of PeLEDs could be important in offering life-like experiences to consumers. Future efforts in PeLEDs could also be directed to investigating the possibility of manufacturing micro-PeLEDs.

Acknowledgements

Dr. He Liu
Dr. Michael Worku
Dr. Azza Ben-Akacha
Dr. Maya Chaaban
Dr. Sujin Lee
Dr. Tunde Blessed Shonde
Dr. Animesh Mondal
Dr. Qingquan He
Dr. Liang-jin Xu
Oluwadara Olasupo
Md Sazedul Islam
Tarannuma F. Manny
Dr. Xinsong Lin, FSU
Dr. J.S. Raaj Vellore Winfred, FSU
Dr. Yan Xin, FSU
Dr. Sam Mao, FSU
Dr. Eric Lochner, FSU
Dr. Kenneth Hanson, FSU