Enhancing LiFi and Lighting: Cs4PbBr6 Zero-Dimensional Perovskite and Quantum Dot Based Color Converters

PROBLEM STATEMENT

Data and wireless communications have been the backbone of technological development for the last two decades. WiFi, the most popular form of wireless communications, has been used widely due to the rise of smart devices such as smartphones and tablets. However, WiFi is disadvantageous as it can be unreliable due to its vulnerability to external sources such as weather, and can lack security thus putting sensitive information, such as bank and government information, at risk. With the development of numerous smart devices and the global rise of the need for greater bandwidth and secure data connections, it becomes critical to find alternative methods for wireless communication. Visible light communications (VLC) is an emerging technology that has been proposed as an alternative to wireless communications. Light Fidelity (LiFi), an upcoming type of VLC, is advantageous due to its properties of extreme speed, security, and reliability under lab conditions. However, the commercial Light Emitting Diodes (LEDs) used by LiFi relatively restrict speed due to the presence of phosphor in them, deeming them unfit for commercial use.

PURPOSE

This research introduces CsPbBr3 zero-dimensional perovskites (0-D) and quantum dots (QDs) into optoelectronics for the first time as color converters with phosphor to:

1- **Decrease phosphor's response time** to the On/Off Keying (OOK) process, resulting in higher bandwidths and frequencies of internet.
2- **Produce warm white light** for multi-functional optoelectronic technologies like LiFi.

This aims to improve the optoelectronic qualities of phosphor based LEDs and streamline the development of optical wireless communication devices, in order to provide more powerful connections and increased data security commercially.

PRELIMINARIES

LiFi is a type of VLC which uses LEDs to transmit data. It promises faster connections and has the potential to transfer up to 100 GB/s under lab conditions, 100x faster than WiFi's 1GB/s maximum.[1] It provides more secure connections as LiFi uses light waves that cannot penetrate walls, thus limiting the data transmission to a confined space and increasing its security.

Figure 1. LiFi concept diagram

Currently, the most cost-efficient white LEDs utilize a blue LED and a down-converting (as seen in figure 2) phosphor with green and red components to produce white light. However, these commercial phosphors have drawbacks, such as:

1- **Long excitation lifetimes** that reduce the on/off keying process and reduces data transmission speed. [2]
2- **Low bandwidth for data transmission**, providing an average frequency of 5 MHz for the phosphor. [4]
3- **Poor quality white lighting,** with cool temperatures that tend to look blue.

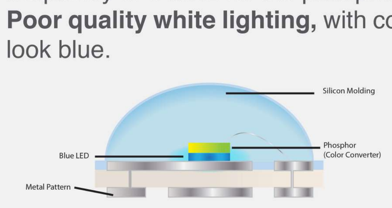


Figure 2. Structure of LED

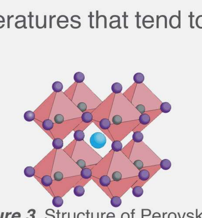


Figure 3. Structure of Perovskite (Martin et al, 2014)

This research uses $CsPbBr_3$ 0-D perovskites and the liquid form of perovskites, Quantum Dots as catalysts for phosphor. They are distinct from other phases, due to their high luminescence and short excitation lifetime (described in Table 1) which can be used to tune the color converting layer.

Table 1 . Characteristics of perovskites used in this research [3]

	0-D	QD
Excitation Lifetime	4 ns	7 ns
Emission	Green	Red

EXPERIMENTAL DESIGN

Sample Strips Composition

1- **Synthesize** of 0-D Perovskites and characterize its properties using X-Ray diffraction.
2- **Manufacture** testable strips using a PDMS base with different ratios of 0-D, QD, and phosphor. as shown in Table 2 where:

A,B,C will represent the different amounts of 0-D

1,2,3,4 will represent the different compositions

Table 2. Content breakdown for samples

Sample Name	0-D $CsPbBr_3$ Perovskite (mg)	Ratio between Silicon and 0-D Perovskite	Commercial Red Phosphor (mg)	$CsPb(I_{0.4}Br_{0.6})_3$ Quantum Dot (µl)
A1	100	1:0.5	0	0
B1	200	1:1	0	0
C1	300	1:1.5	0	0
A2	100	1:0.5	0	10
B2	200	1:1	0	10
C2	300	1:1.5	0	10
A3	100	1:0.5	100	0
B3	200	1:1	100	0
C3	300	1:1.5	100	0
A4	100	1:0.5	100	10
B4	200	1:1	100	10
C4	300	1:1.5	100	10

Testing Parameters

1- **Test** the strips for warm white light production through a spectrometer using the **Color Rendering Index (CRI)** and **Color Correlated Temperature (CCT)** as determining factors.
2- Test the strips for **modulation frequency** and **data transmission stability** using a Mixed Domain Oscilascope.

Testing Predictions

1- An accelerated excitation lifetime for the phosphor, which would lead to an increase in modulation frequency of 5Mhz<
2- The production of warm white light with CRI of 80< and CCTs within the warm light range 2700K - 3000K.

Main Materials

- Cesium Bromide (CsBr), Purity 99.9%
- Lead Bromide (PbBr2), Purity 98%
- CsPb(I0.4Br0.6)3 QD solution
- Polydimethylsiloxane (PDMS)
- Bruker AXS D8 X-Ray Diffractometer (XRD)
- Dimethyl Sulfoxide (DMSO)
- Phosphorous
- Mixed Domain Oscilloscope
- GL Spectis 5.0 Touch Spectrometer

Figure 4. Chemical materials used in testing

PROCEDURES

Synthesis of 0-D CsPbBr3

1- **Synthesis** occurred as CsBr and PbBr2 was dissolved in DMSO. After a heating process from 60C to 120C, the precipitation (as seen in figure 4) was collected, washed, and finally left to dry in the vacuum.
2- **Characterization** was done using a Bruker AXS D8 X-Ray Diffractometer with a scan rate of 5° from 8° to 50° to confirm purity and phase. The data collected confirmed the material's phase and purity as seen in figure.

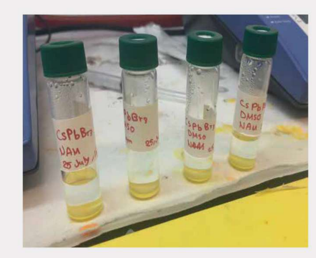
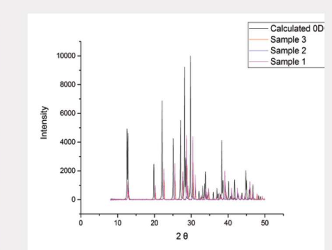


Figure 5. Percipitation during synthesis



Graph 1. XRD peaks for samples

Manufacturing Testable Strips Using PDMS

1- The produced 0-D perovsites were embedded in PDMS at different ratios to the PDMS. **(A_, B_, C_)**
2- **Control Samples** were made with a base sample from the previous step (**Sample _1**), as seen in figures 6 and 7, and a base sample with the addition of QDs (**Sample _2**) to be used for comparative analysis.
3- **Test Samples** were made by distributing phosphor on the base samples **(Sample _3)**, as seen in figures 8 and 9, and by adding QDs to the aforementioned sample **(Sample _4)**.

This led to a total of 12 samples for this research as detailed in Table 1.

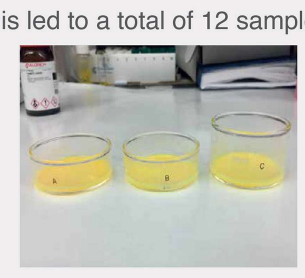


Figure 6. Control Sample _1 in all variations.

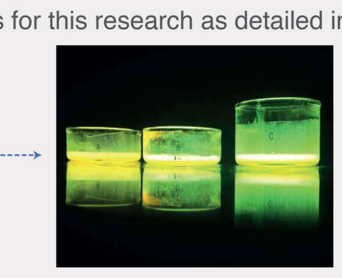


Figure 7. Samples _1 under UV light displaying green luminescence

Figure 8. sample A3 with the addition of phosphor

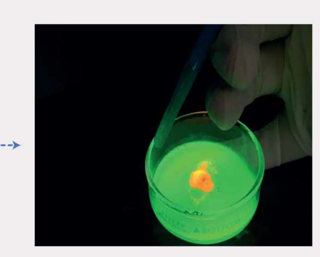


Figure 9. Sample A3 unmixed under UV displaying red luminescence of phosphor

Characterization of Modulation Frequency and White Light Properties

1- **Modulation Frequencies and Stability** were calculated using a setup which consisted of a blue laser diode, filter, and a mixed domain oscilloscope over different time intervals and excitation periods.
2- **White lighting properties** were measured by calculating the CRI and CCT using a blue laser diode and a GL spectis 5.0 touch spectrometer as seen in the setup in figure.

Samples 1 ad 2 results were not recreated due extremely poor performances

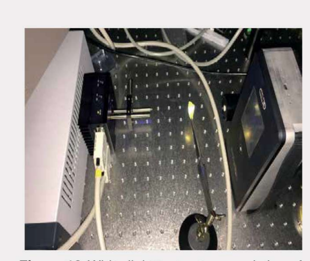


Figure 10. White light test setup consisting of a blue LD and a GL Spectis 5.0 Touch spectrometer.

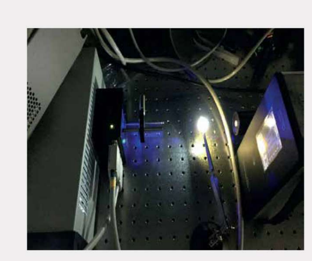
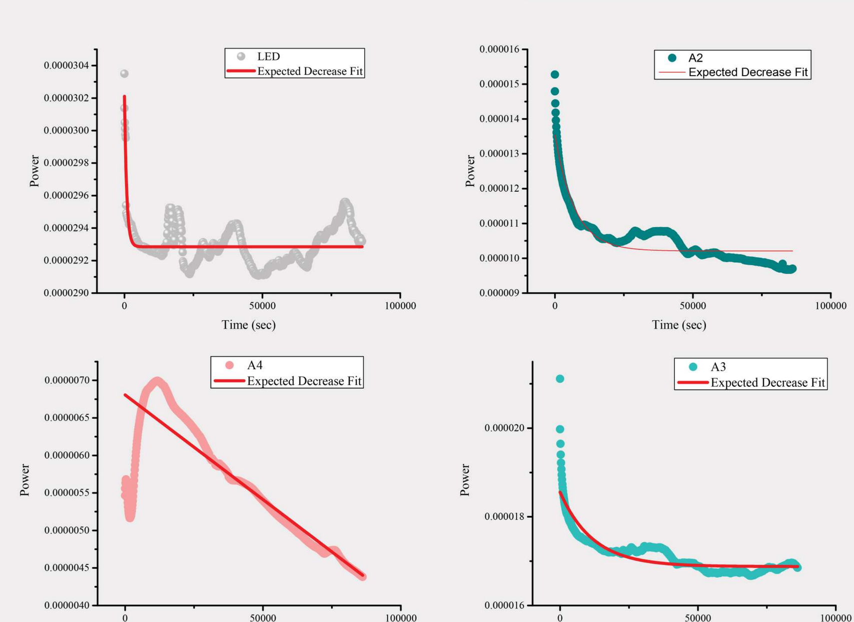


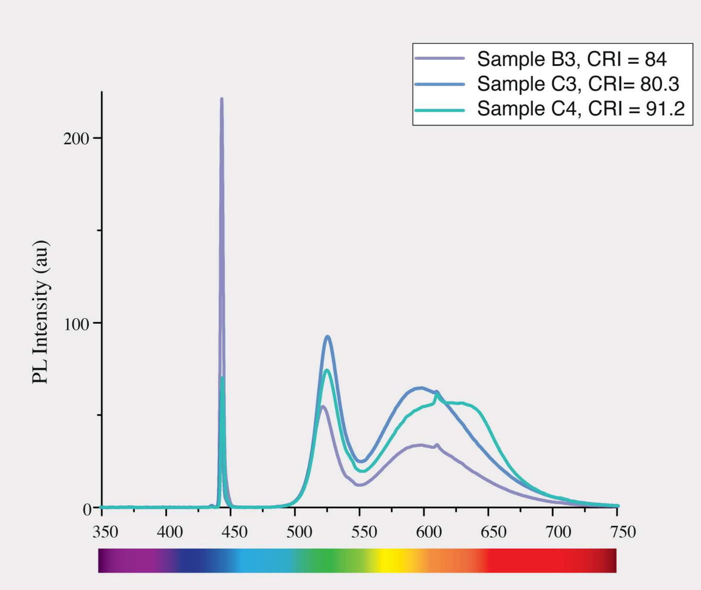
Figure 11. White light test in progress.

DATA AND GRAPHS



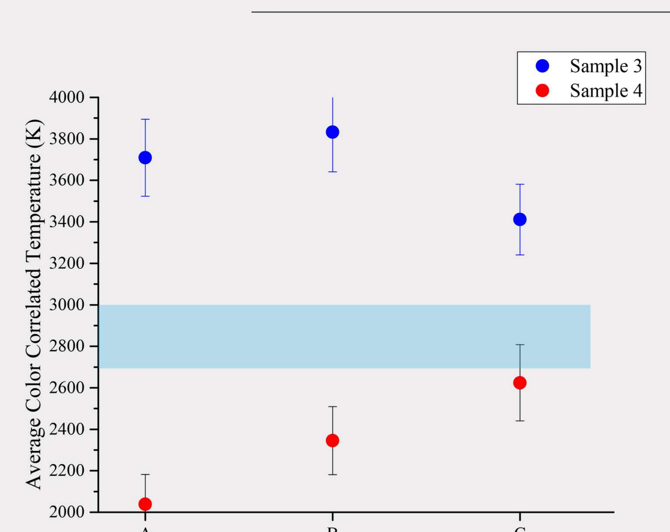
Graph 2 . Data transmission stability for A samples.

Samples A2 and A3 , which both contain 0-D, were more stable than commercial LED, while A4, with the QDs, was less stable.



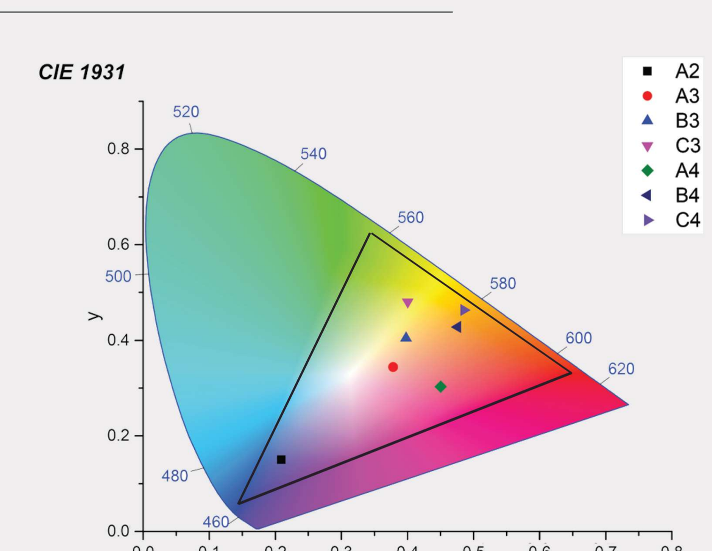
Graph 3. White light (RGB) Spectrums for samples B3, C3, C4 .

The addition of different components throughout the sample was reflected by the different emission rates, suggesting tunability.



Graph 4. Average CCT for each sample against the targeted range for warm white light (2700k-3000k)

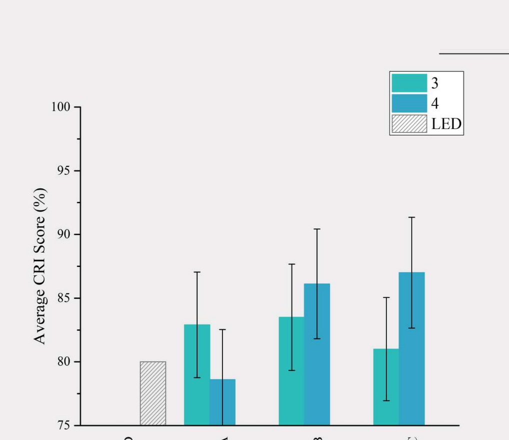
The samples with only 0-D (Sample 3) had high temperatures and produced cool light. However the addition of QDs in Sample 4 resulted in lower temperatures and warmer light.



Graph 5. CIE 1931 color coordinates for selected research samples against white color region

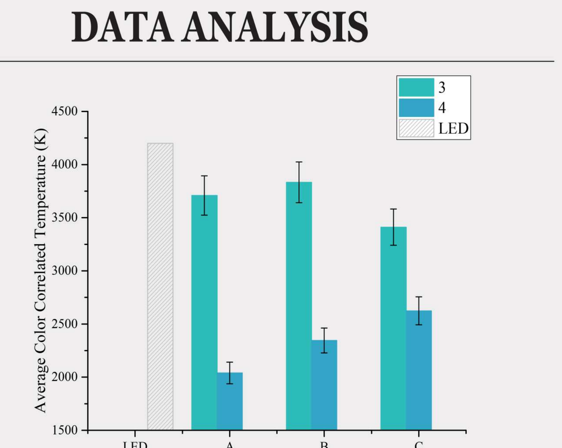
Multiple samples fell within the white light region with A3 being the closest to pure white.

DATA ANALYSIS



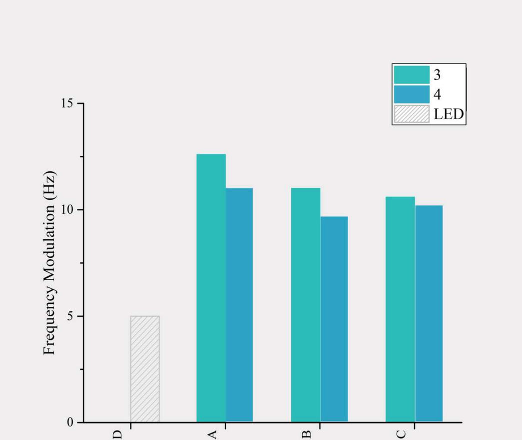
Graph 6. Commercial LED CRI vs Test Samples CRI

Samples 3 persistenly showed higher CRIs than the LED. While A4 showed a decrease in CRI with the addition of the QD, the rest of Samples 4 had greaters CRIs than the LED and samples 3.



Graph 7. Commercial LED CCT vs Test Samples CCT

Both samples 3 and 4 had lower temperatures than LED, however, sample C4 had temperatures within warm light range.



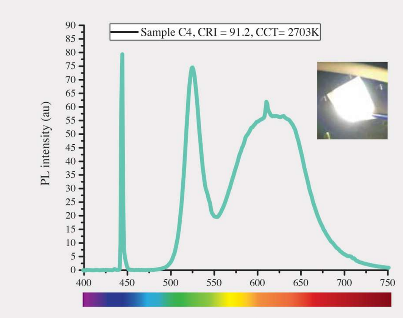
Graph 8. Commercial LED modulation frequency vs test samples

The samples had higher frequency modulation rates than the LED.

RESULTS

- A CRI of 91.2 was attained in sample C4 with a CCT of 2703K as seen in graph 9.
- There was an increase in CRI and CCT in most samples compared to commercial LED CRI and CCT rates.

QD > 0-D > LED



Graph 9. White light (RGB) Spectrum for sample C4 presenting the best research sample

- Modulation Frequency was produced at double the rate of commercial frequency (5 Mhz) ranging from 10-12.6 MHz
- 0-D samples showed an increased stability when compared with compared commercial LED data transmission stability.

0-D > LED > QD

CONCLUSIONS

The projects predictions were confirmed as :-

- The use of 0-D successfully reduced the response time of the phosphor within the color converting layer,thus producing higher frequency rates than commercial LEDs.
- The addition of both 0-D and QD allowed for the tunaibility of warm white light, where it helped increase the CRI and decrease the CCT towards the warm range.

APPLICATIONS

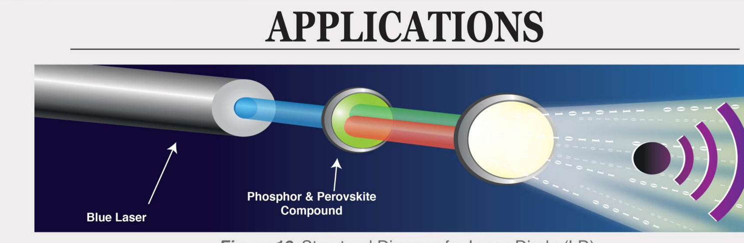


Figure 12. Structural Diagram for Laser Diode (LD)

$CsPbBr_3$ 0-D perovskites and quantum dots exhibit many physical and chemical properties, such as photoluminescence and short excitation lifetimes, that can be utilized in photovoltaics, optoelectronics and, other fields of material science. In the optoelectronic field, these materials can be used to produce coatings for laser diodes particular to optical wireless connections, more specifically, visible light communications such as LiFi.

Following the development of the right materials, the implementation of LiFi will be manageable and cost effective as it will work using pre-existing internet providing infrastructures such as Ethernet or fiber optics. It will provide users with secure and stable internet connections, replacing other forms of wireless communications.

COST ANALYSIS

Table 3. Cost breakdown for research samples

Name	Amount/Unit	Price/Unit	Price/ Amount used per batch
Lead(II) bromide - 99.999% trace metals basis	5 grams	69.89 USD	51.2 USD
Cesium bromide - 99.9% trace metals basis	100 grams	253.72 USD	5.39 USD
Dimethyl sulfoxide - ACS reagent, ≥99.9%	100 ml	24.34 USD	2.34 USD
Poly(dimethylsiloxane) analytical standard	25 grams	239.29 USD	19.14 USD
Commercial Phosphor	1 gram	2-4 USD	0.4 USD
Total/ Batch			78.47 USD

Through the measurements refrenced in Table 3, a batch can create roughly 684 color converting films (5mm in size) for LEDs which makes the actual cost of the LED (with the color converter) **8.7 USD** compared to the cost of commercial LEDs which range from **4-7 USD** depending on wattage.

With developing methods of producing 0-D, such as the methodology mentioned by Chen et al [9] , costs are expected to decrease by a couple of dollars due to increased yield during synthesis and less product loss due to impurities.

FUTURE WORK

Short Term

Resume the testing of different ratios of $CsPbBr_3$ 0-D perovskites, Quantum dots and phosphor in order to create a compound that fulfills the optoelectronic qualities needed for commercial implementation of LiFi LDs.

These optoelectronic qualities mandate that:

The ratio maintains high levels of warm white light with CRIs above 80 and CCTs within the warm light range of (2700K°-3000K°).

The ratio maintains high bandwidths of approximately 400 MHz with high, long lasting stability for data transmission.

Long Term

Once an optimal ratio is found and a compound is created, it will be manufactured to produce LD coatings for the commercial implementation of LiFi.

REFERENCES

[1] Baykas, Tuncer, Chin-Sean Sum, Zhou Lan, Junyi Wang, M. Rahman, Hiroshi Harada, and Shuzo Kato. "IEEE 802.15.3c: The First IEEE Wireless Standard for Data Rates over 1 Gb/s." IEEE Communications Magazine 49, no. 7 (2011): 114-21. Accessed August 19, 2016. doi:10.1109/mcom.2011.5936164.
[2] Dursun, Ibrahim, Chao Shen, Manas R. Parida, Jun Pan, Smritakshi P. Sarmah, Davide Priante, Noktan Alyami, Jiakai Liu, Makhsud I. Saidaminov, Mohd S. Alias, Ahmed L. Abdelhady, Tien Khee Ng, Omar F. Mohammed, Boon S. Ooi, and Osman M. Bakr. "Perovskite Nanocrystals as a Color Converter for Visible Light Communication." ACS Photonics 3, no. 7 (2016): 1150-156. Accessed July 24, 2016. doi:10.1021/acsphotonics.6b00187.
[3] Saidaminov, Makhsud I., Jawaher Almutlaq, Smritakshi Sarmah, Ibrahim Dursun, Ayan A. Zhumekenov, Raihana Begum, Jun Pan, Namchul Cho, Omar F. Mohammed, and Osman M. Bakr. "Pure Cs4PbBr6: Highly Luminescent Zero-Dimensional Perovskite Solids." ACS Energy Letters 1, no. 4 (2016): 840-45. Accessed July 22, 2016. doi:10.1021/acsenergylett.6b00396.
[4] Sajjad, Muhammad T., Pavlos P. Manousiadis, Hyunchae Chun, Dimali A. Vithanage, Sujan Rajbhandari, Alexander L. Kanibolotsky, Grahame Faulkner, Dominic O'Brien, Peter J. Skabara, Ifor D. W. Samuel, and Graham A. Turnbull. "Novel Fast Color-Converter for Visible Light Communication Using a Blend of Conjugated Polymers." ACS Photonics 2, no. 2 (2015): 194-99. Accessed July 23, 2016. doi:10.1021/ph500451y.
[5] Tuo, Jiabin, B. Corbett, and H. Shams. "Visible Light Communication by Using Commercial Phosphor Based White LEDs." IET Irish Signals and Systems Conference (ISSC 2012), 2012. Accessed July 23, 2016. doi:10.1049/ic.2012.0227.
[6] Tsonev, Dobroslav, Stefan Videv, and Harald Haas. "Towards a 100 Gb/s Visible Light Wireless Access Network." Optics Express 23, no. 2 (2015): 1627. Accessed July 21, 2016. doi:10.1364/oe.23.001627.
[7] Cook, Emily, Ruby Fong, Julie Horrocks, David Wilkinson, and Robert Speller. "Energy Dispersive X-ray Diffraction as a Means to Identify Illicit Materials: A Preliminary Optimisation Study." Applied Radiation and Isotopes 65, no. 8 (2007): 959-67. Accessed August 22, 2016. doi:10.1016/j.apradiso.2007.02.010.
[8] Borbély, Ákos, Árpád Sámson, and János Schanda. "The Concept of Correlated Colour Temperature Revisited." Color Research & Application Color Res. Appl. 26, no. 6 (2001): 450-57. Accessed August 17, 2016. doi:10.1002/col.1065.
[9]Chen, Daqin, Zhongyi Wan, Xiao Chen, Yongjun Yuan, and Jiasong Zhong. "Large-scale room-temperature synthesis and optical properties of perovskite-related Cs4PbBr6 fluorophores." J. Mater. Chem. C 4, no. 45 (2016): 10646-0653.

*All graphs and photos by researcher unless otherwise noted.