Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for:

3D-Printed Alternating Current Electroluminescent Devices

Cole D. Brubaker,[†] Kailey N. Newcome,[†] G. Kane Jennings,[▽,*] Douglas E. Adams[†,⊥,*]

Departments of [†]Civil and Environmental Engineering, [▽]Chemical and Biomolecular Engineering, [⊥]Mechanical Engineering Vanderbilt University, Nashville, Tennessee 37235, United States.

Corresponding Authors

*Douglas Adams: douglas.adams@vanderbilt.edu
* G. Kane Jennings: kane.g.jennings@vanderbilt.edu

Experimental Details – Materials and Methods

Materials

Metal doped phosphor powder was purchased from Fulcom (Marshal) Company Limited (LP-6842) and used as received without any further modifications. The ZnS:Cu phosphor powder, with an approximate particle size of 24 ± 6 μm (Figure S1), emits a bright blue/green coloration under UV excitation. Polylactic acid pellets (3D850) were purchased from Filabot and supplied by Natureworks. Conductive PLA filament was purchased from Proto-Pasta. ITO-coated glass slides were purchased from Delta Technologies (Part No. CG-51IN-1115). ACS grade dichloromethane and all other solvents used in this study were purchased from Fischer Scientific and used without any further modification.

Filament Fabrication

Electroluminescent, phosphor doped filament was fabricated according to previously described protocols.[1,2] In short, the following procedure was used. A desired amount of polylactic acid polymer host matrix was dissolved in dichloromethane under stirring. Upon complete dissolution, phosphors were added to the solution at a predetermined weight-percent and the mixture was allowed to stir until a homogenous mixture was obtained. Next, the PLA/phosphor mixture was transferred to crystallization dishes and dried overnight under ambient conditions. Upon complete removal of the solvent, the resultant hard plastic was shredded to obtain small pellets. The pellets were then further dried at 100°C to remove any remaining solvent and extruded at 180°C using a Filabot EX2 extrusion system. The PLA/phosphor filament was cooled with a water bath and spooled prior to sample fabrication and 3D printing.

Sample and ACEL Device Fabrication

All samples studied in this report were fabricated using a dual nozzle Ultimaker 3 Extended FDM type desktop printer. PLA/phosphor filament was extruded through at 0.4 mm nozzle at 215°C and deposited onto a glass build plate heated to 60°C. A print layer height of 0.1 mm (100 μm) was used for all samples. For the fabrication of the 3D-printed electroluminescent devices, PLA/phosphor filament was printed onto a conductive ITO-coated glass slide, upon which carbon-based conductive PLA filament was deposited directly on top using the same processing temperatures and conditions previously described (structure of ACEL device from bottom to top: ITO glass slide/3D-printed PLA/phosphor layer/3D-printed conductive PLA electrode). Prior to device fabrication, ITO slides were washed in an ultrasonic bath for 30 mins in a mixture of ethanol/acetone/chloroform (2/1/1 v/v/v), rinsed with DI water, and further washed in an ultrasonic bath for an additional 30 minutes in an aqueous solution containing 2% KOH.[3,4] Clean ITO slides were stored in DI water and dried with nitrogen prior to sample fabrication and 3D printing.

Characterization and Materials Testing

Materials characterization and testing was performed as follows. Differential interference contrast (DIC) and white light microscopy were recorded using a Zeiss Axiovert 200 Inverted Fluorescence Microscope at various ranges of magnification. Representative photoluminescence (PL) spectra for 3D-printed PLA/phosphor thin films was recorded using a PTI spectrofluorometer with an excitation wavelength of 400 nm and accompanying software. A custom stand was used to support 3D-printed thin films during testing to ensure uniformity between individual scans. A total of three scans for each weight percent studied were recorded to evaluate the uniformity of the optical response for the as-printed thin film samples. Spectral data for the 3D-printed electroluminescent devices under various excitation conditions were recorded using a CDS 600 CCD-based spectrometer with an integration time of 2.5 s and accompanying software. 3D-printed ACEL devices were excited using a Keysight 10MHz function generator and Krohn-Hite voltage amplification system (model 7500). In total, five individual 3D-printed ACEL devices were tested. Still images and videos of the devices were collected using a Cannon EOS 6D camera.

Figures

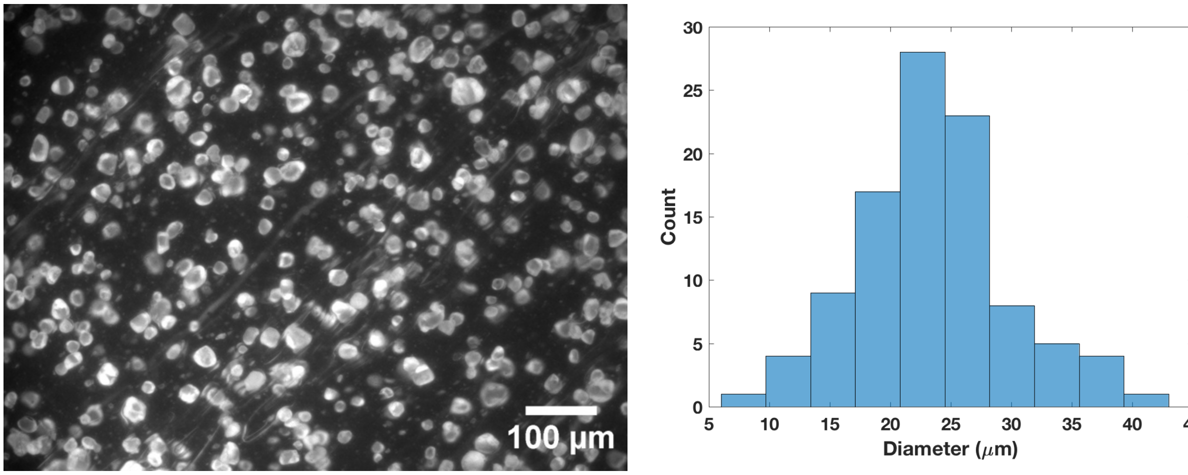

Figure S1. WL microscopy of ZnS:Cu phosphors in PLA, and corresponding size distribution. Average diameter is 24 ± 6 μm.

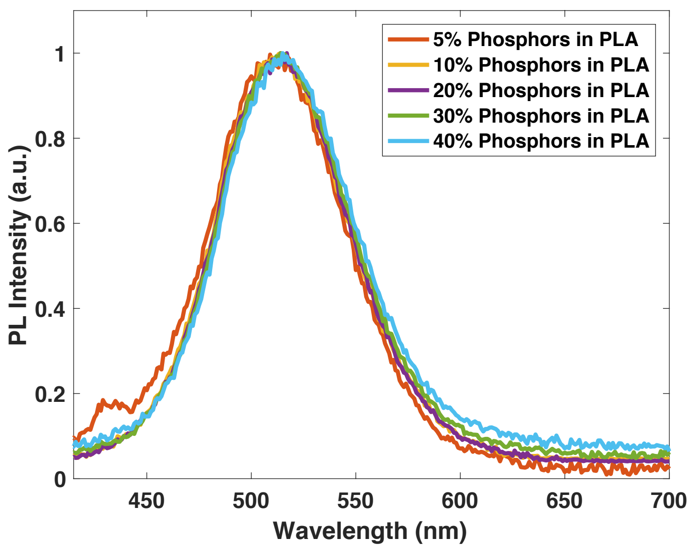

Figure S2. Normalized PL spectral response for 3D-printed PLA/phosphor thin film samples at various concentrations of phosphors in PLA by weight.

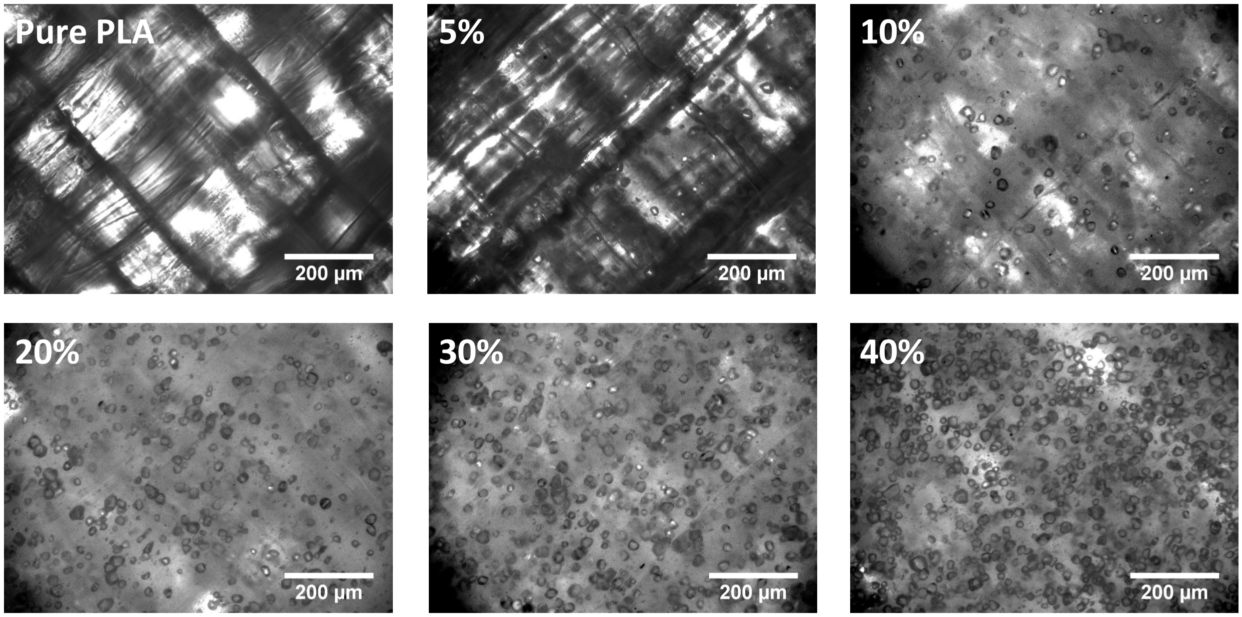

Figure S3. DIC microscopy of 3d-printed PLA/phosphor thin film samples at various concentrations of phosphors in PLA by weight. With increasing concentration, phosphors are observed to exist in close proximity, often in contact with one another at higher concentrations of embedded phosphors. The diagonal lines are a result of the sample fabrication process and nozzle movement/filament deposition during the 3D printing process.

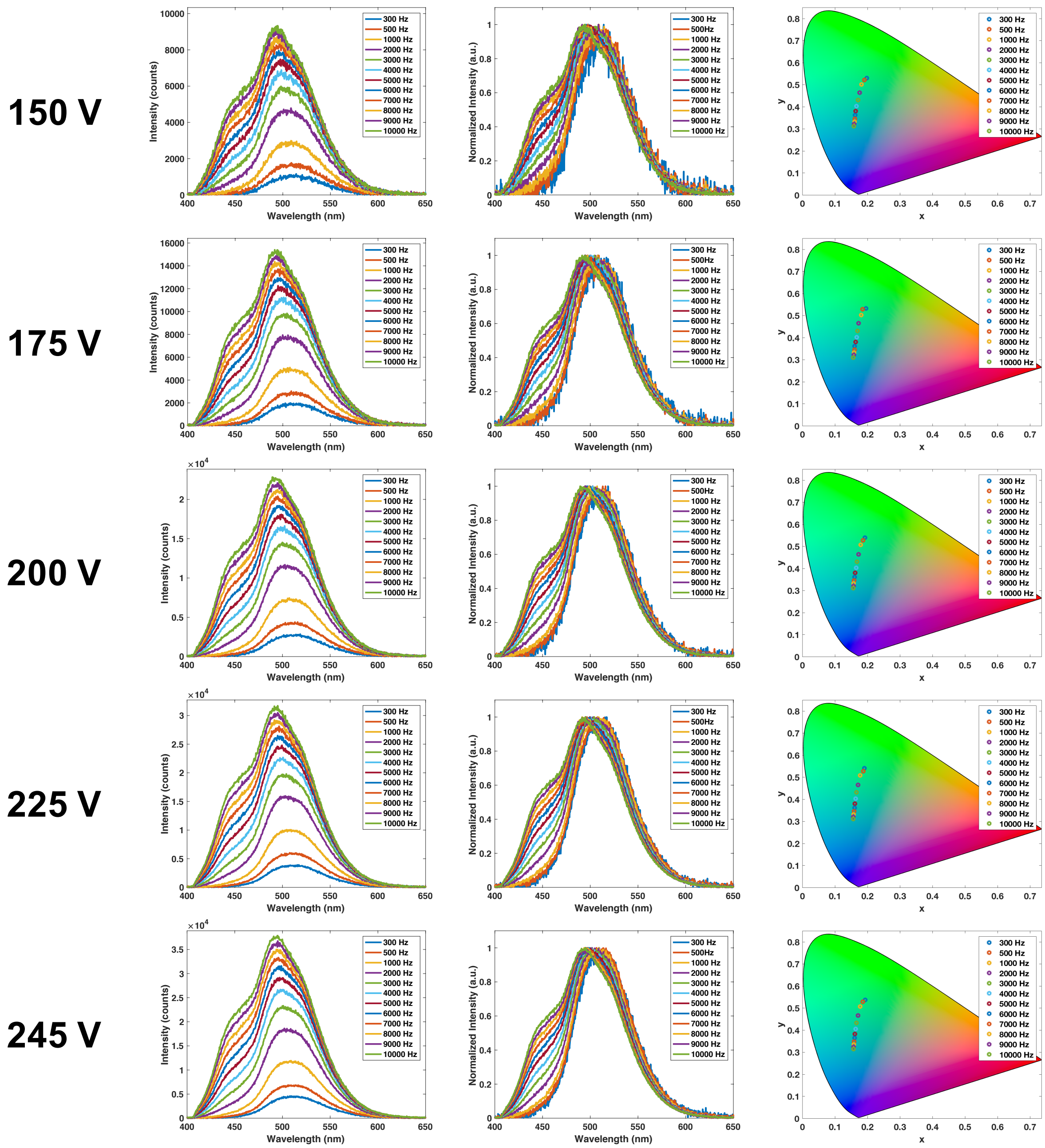

Figure S4. Frequency-dependent as-recorded and normalized spectral response (left and middle columns) of a 3D-printed ACEL device at various excitation voltages and corresponding CIE coordinates (x,y) (right column). Data shown for 245 V excitation is the same as that shown in Figure 3.

Table S1. Frequency-dependent response of CIE coordinates (x,y) at various applied voltages. CIE coordinates (x,y) correspond to data shown in Figure S4.

	150 V		**175 V**		**200 V**		**225 V**		**245 V**	
Frequency (Hz)	**x**	**y**	**x**	**y**	**x**	**y**	**x**	**y**	**x**	**y**
50	0.272	0.443	0.230	0.504	0.235	0.516	0.218	0.542	0.214	0.549
100	0.235	0.509	0.216	0.526	0.213	0.528	0.214	0.532	0.208	0.547
300	0.198	0.530	0.195	0.532	0.192	0.539	0.191	0.540	0.193	0.537
500	0.190	0.521	0.185	0.529	0.187	0.527	0.187	0.527	0.186	0.528
1000	0.182	0.502	0.181	0.502	0.179	0.507	0.178	0.508	0.177	0.507
2000	0.176	0.464	0.173	0.465	0.172	0.464	0.171	0.465	0.171	0.466
3000	0.171	0.431	0.169	0.430	0.168	0.431	0.166	0.431	0.166	0.432
4000	0.166	0.403	0.167	0.402	0.165	0.403	0.164	0.403	0.164	0.405
5000	0.164	0.380	0.163	0.380	0.162	0.380	0.162	0.380	0.161	0.382
6000	0.162	0.362	0.161	0.361	0.161	0.361	0.160	0.361	0.161	0.364
7000	0.161	0.346	0.160	0.345	0.159	0.345	0.159	0.345	0.159	0.348
8000	0.160	0.332	0.159	0.332	0.158	0.332	0.158	0.332	0.158	0.335
9000	0.159	0.321	0.158	0.321	0.157	0.320	0.157	0.320	0.157	0.324
10000	0.158	0.311	0.157	0.310	0.157	0.310	0.156	0.310	0.157	0.314

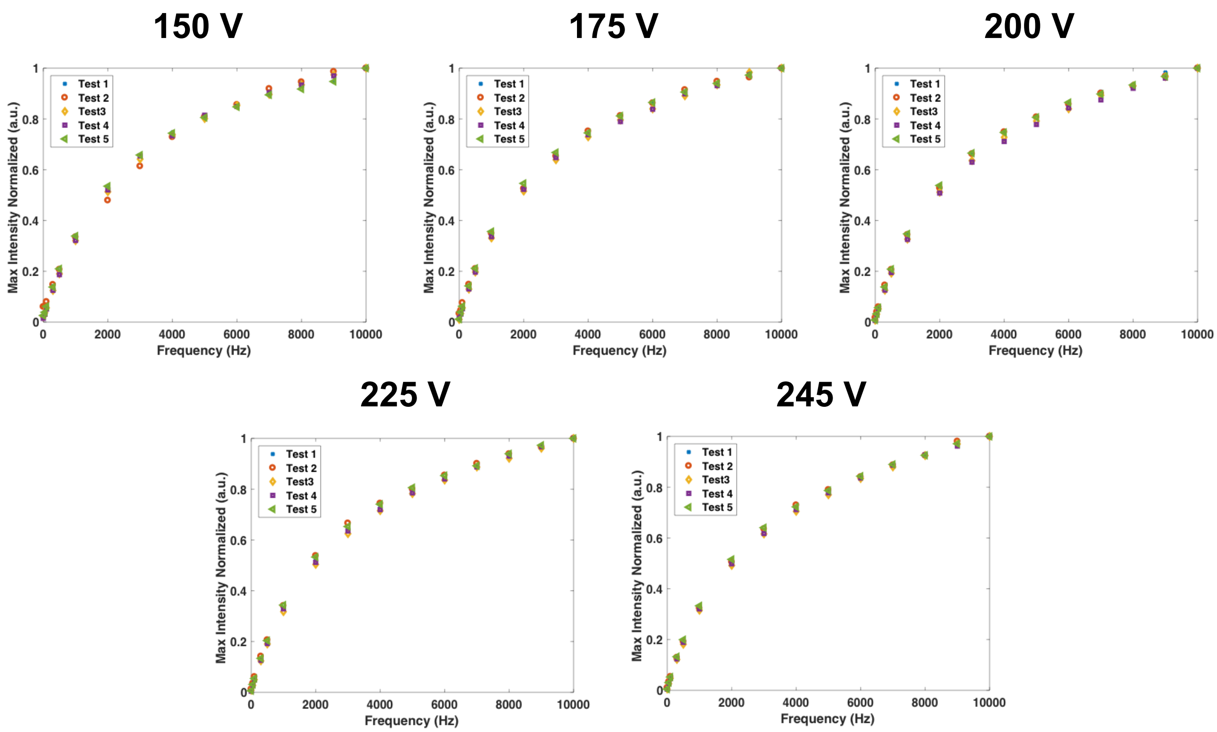

Figure S5. Normalized frequency-dependent maximum EL response at various applied voltages for five individual test samples studied. Overall electroluminescent response was found to be highly reproducible between individual samples for all voltages tested.

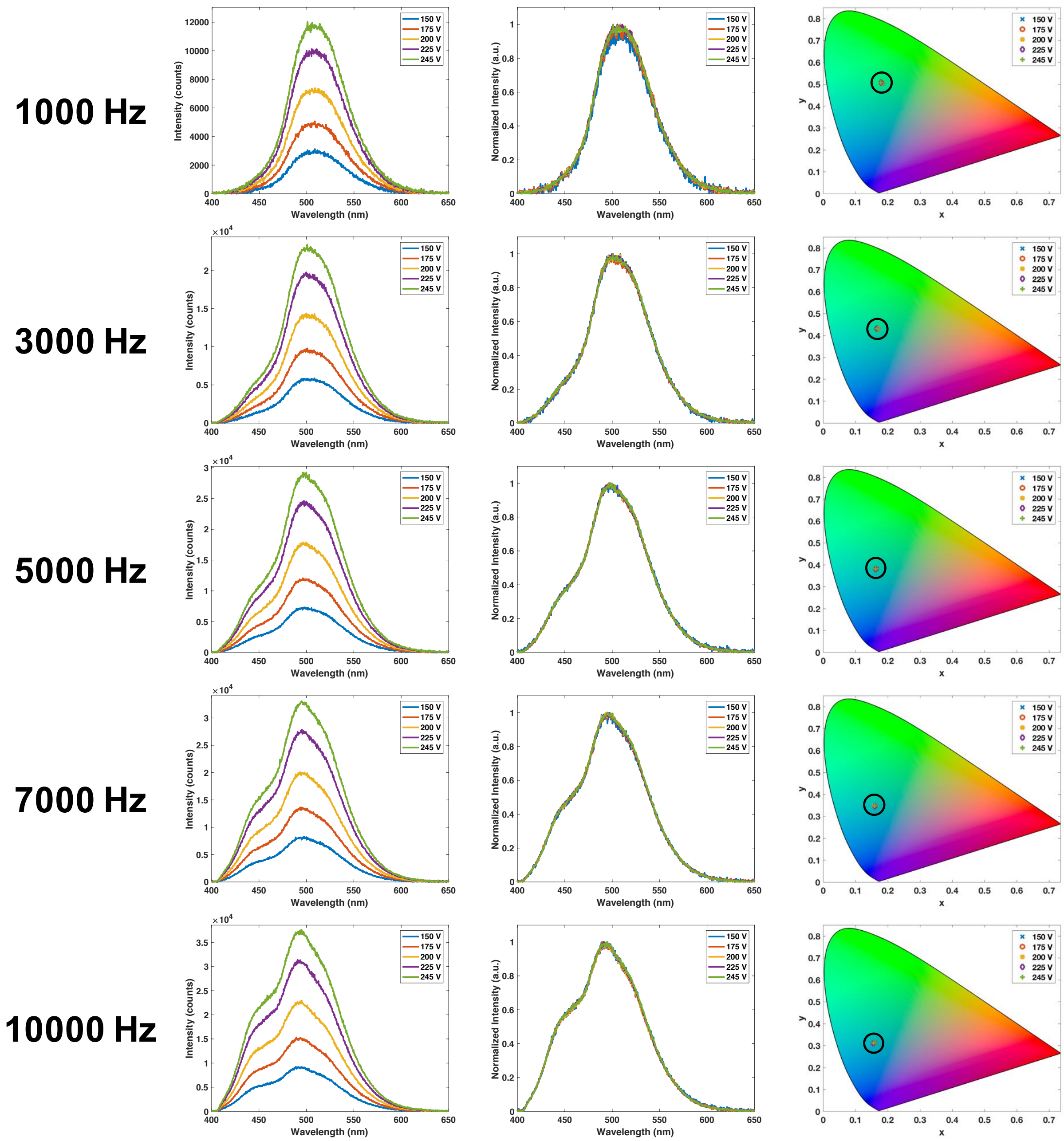

Figure S6. Voltage-dependent as-recorded and normalized spectral response (left and middle columns) of a 3D-printed ACEL device at various excitation frequencies and corresponding CIE coordinates (x,y) (right column). Data shown for 10000 Hz excitation is the same as that shown in Figure 3.

Table S2. Voltage-dependent response of CIE coordinates (x,y) at various applied frequencies. CIE coordinates (x,y) correspond to data shown in Figure S6.

	1000 Hz		3000 Hz		5000 Hz		7000Hz		10000 Hz	
Voltage (V)	**x**	**y**	**x**	**y**	**x**	**y**	**x**	**y**	**x**	**y**
150	0.183	0.504	0.170	0.431	0.166	0.381	0.161	0.348	0.160	0.312
175	0.181	0.505	0.169	0.430	0.163	0.381	0.160	0.346	0.157	0.311
20	0.180	0.505	0.168	0.431	0.162	0.381	0.159	0.346	0.156	0.311
225	0.179	0.507	0.166	0.431	0.162	0.380	0.159	0.345	0.156	0.310
245	0.179	0.507	0.167	0.432	0.162	0.382	0.159	0.348	0.156	0.313

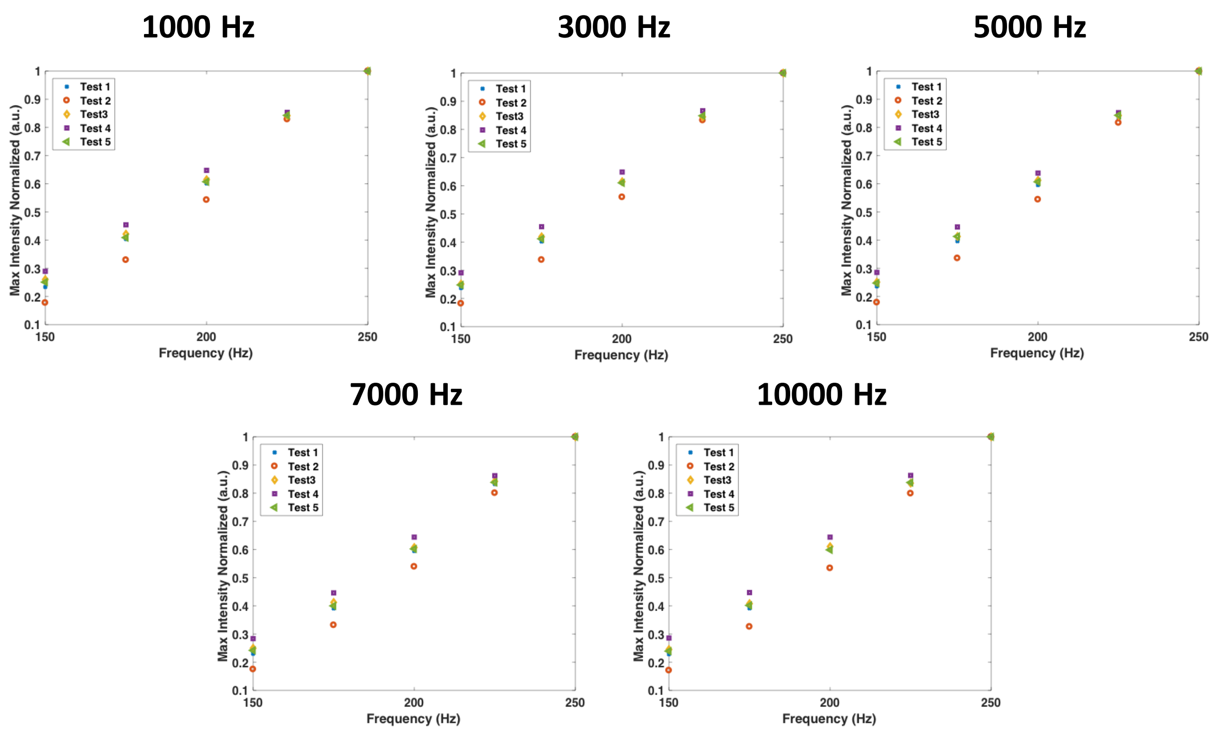

Figure S7. Normalized voltage-dependent maximum EL response at various applied frequencies for five individual test samples studied. Overall electroluminescent response was found to be highly reproducible between individual samples for all frequencies tested.

Table S3. Curve fitting data for voltage-dependent maximum EL response at various frequencies. Data was fit with a linear model using the following equation: y(x) = p1*x+p2.

Frequency (Hz)	**p1**	**p2**	**R-Squared**
100	12.57	-1341	0.9969
500	56.8	-6992	0.9965
1000	95.13	-11380	0.9965
3000	187.1	-22600	0.9972
5000	234.5	-28440	0.9954
7000	265.8	-32310	0.9961
10000	303	-37010	0.9969

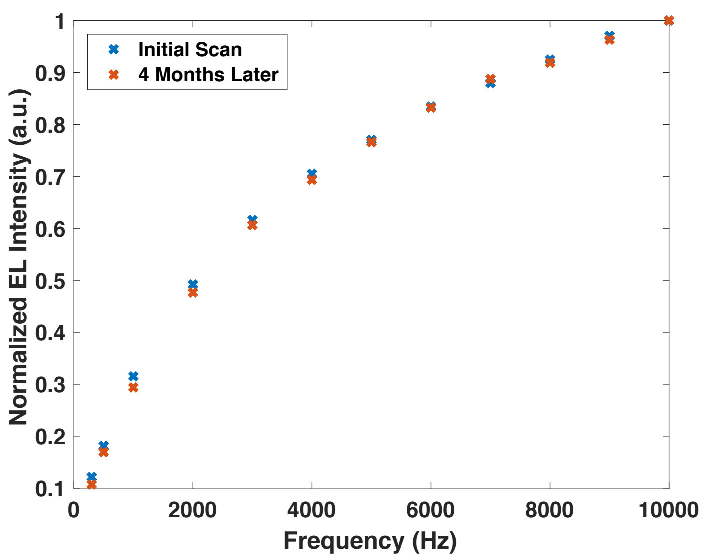

Figure S8. Comparison of normalized frequency-dependent maximum EL response for 3D-printed ACEL device up to four months after printing, where no change in the recorded spectral behavior was observed.

References

(1) Brubaker, C. D.; Davies, M. A.; McBride, J. R.; Rosenthal, S. J.; Kane Jennings, G.; Adams, D. E. Nondestructive Evaluation and Detection of Defects in 3D Printed Materials Using the Optical Properties of Gold Nanoparticles. *Appl. Nano Mater.* **2018**, *1* (3), 1377–1384.

(2) Brubaker, C. D.; Frecker, T. M.; McBride, J. R.; Reid, K. R.; Jennings, G. K.; Rosenthal, S. J.; Adams, D. E. Incorporation of Fluorescent Quantum Dots for 3D Printing and Additive Manufacturing Applications. *J. Mater. Chem. C* **2018**, *6* (28), 7584–7593.

(3) He, J.-A.; Samuelson, L.; Li, L.; Kumar, J.; Tripathy, S. K. Oriented Bacteriorhodopsin / Polycation Multilayers by Electrostatic Layer-by-Layer Assembly. *J. Phys. Chem. B* **1998**, *102*, 7067–7072.

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