REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)
08-03-2021

2. REPORT TYPE
Final Report

3. DATES COVERED (From - To)
1-Jun-2019 - 29-Feb-2020

4. TITLE AND SUBTITLE
Final Report: Designing Wavelength-Specific Visible Light Photocurable Resins

5a. CONTRACT NUMBER
W911NF-19-1-0310

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

6. AUTHORS

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES

University of Texas at Austin
101 East 27th Street
Suite 5.300
Austin, TX 78712 -1532

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
74198-CH-II.3

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Zachariah Page
a. REPORT	b. ABSTRACT	c. THIS PAGE			
UU	UU	UU	UU		19b. TELEPHONE NUMBER 512-232-2462

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

RPPR Final Report
as of 02-Sep-2021

Agency Code: 21XD

Proposal Number: 74198CHII **Agreement Number: W911NF-19-1-0310**
INVESTIGATOR(S):

Name: Zachariah Allen Page
Email: zpage@cm.utexas.edu
Phone Number: 5122322462
Principal: Y

Organization: **University of Texas at Austin**
Address: 101 East 27th Street, Austin, TX 787121532
Country: USA
DUNS Number: 170230239 EIN: 746000203
Report Date: 31-May-2020 Date Received: 08-Mar-2021
Final Report for Period Beginning 01-Jun-2019 and Ending 29-Feb-2020
Title: Designing Wavelength-Specific Visible Light Photocurable Resins
Begin Performance Period: 01-Jun-2019 **End Performance Period:** 29-Feb-2020
Report Term: 0-Other
Submitted By: Zachariah Page Email: zpage@cm.utexas.edu
Phone: (512) 232-2462
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 2 **STEM Participants:** 1

Major Goals: Specific Targets:
1) Optimize blue- and red-light curable epoxy and acrylate resins using a Type I photoacid generator (PAG) and Type II photoredox catalyst (PRC) system (50% completion, red-light curable acrylate accomplished)
2) Identify opaquing agents that are compatible with visible light activated cationic and radical chemistries (100% completion)
3) Interrogate the wavelength-specificity of the newly developed visible light photopolymer resins along with pattern resolution and mechanical performance of the cured materials - (75% completion, patter resolution and mechanical performance of visible light photopolymer resins accomplished, wavelength-specificity partially complete)

Additional goal details: Light has been used to rapidly convert liquid resins into solid objects via photocuring, which has enabled transformative technological advancements in imaging, photolithography, adhesives, coatings, and, most recently, stereolithographic 3D printing. However, in contemporary photolithography and more recently stereolithographic additive manufacturing, high energy UV/violet light (< 420 nm) is used to prepare 2D polymer patterns on surfaces and 3D objects, respectively. The reliance on UV light limits material compatibility due to degradation and attenuation by absorption or scattering of high energy photons. To solve this problem we turned to visible light as a more mild and cost-effective energy source for photocuring, which has been made possible by the recent widespread availability of inexpensive light emitting diodes (LEDs). However, photocuring with visible light is an ongoing challenge that has been restricted to long exposure times (> 60 s) and/or high intensity irradiation (> 50 mW/cm2), precluding their utility in photocuring applications. The tradeoff between reaction rate and incident light intensity necessitated a closer examination of visible-light activated PRCs to advance state-of-the-art photocuring. Furthermore, translation of rapid visible light photocuring to emergent 3D printing technology represented an opportunity to examine the associated fundamental scientific challenges, such as the influence of resin composition and wavelength of light exposure on resolution and mechanical properties of the cured parts. These two unmet needs were examined through a systematic analysis of BODIPY PRCs and digital light processing (DLP) 3D printing with violet, blue, green, and red LEDs.

Accomplishments: Specific Targets:
1) Optimize blue- and red-light curable epoxy and acrylate resins using a Type I photoacid generator (PAG) and Type II photoredox catalyst (PRC) system (50% completion, red-light curable acrylate accomplished)
2) Identify opaquing agents that are compatible with visible light activated cationic and radical chemistries (100% completion)
3) Interrogate the wavelength-specificity of the newly developed visible light photopolymer resins along with

pattern resolution and mechanical performance of the cured materials - (75% completion, patter resolution and mechanical performance of visible light photopolymer resins accomplished, wavelength-specificity partially complete)

Key Results: Structure-property relationships as they pertain to efficient green-to-far red light absorbing BODIPY PRCs (1) and rapid high resolution visible light-based DLP 3D printing with commercial PRCs (2) were examined through the utility of novel three component photosystems. Through this approach, we have gathered the requisite capability and knowledge to facilitate the rational design of multimaterial 3D objects via wavelength-specific photocuring. Thus, the chemistry has informed the materials development, and the materials will enable unique capabilities for the objects they comprise (e.g., joints, actuators, synthetic tissue, and reinforced plastics) with potential utility in state-of-the-art camouflage and protective wear technologies of relevance to the ARO and more generally the Department of Defense missions.

(1). Structure-Property Relationships for Efficient Visible Light Photochemistry. Structure-property relationships of visible light activated PRCs that improve efficiency in photocuring were identified using BODIPY as a scaffold. Key findings include rapid photopolymerizations (complete conversion within ~60 s) at extremely low catalyst loadings (~0.001 mol%) or light intensities (~0.01 mW/cm2 green light or ~1 mW/cm2 far-red light). This was made possible by halogenation of the BODIPY core, which was demonstrated to be an effective strategy to improve photopolymerization efficiency across multiple BODIPY classes (both carbon and nitrogen bridged derivatives) (Figure 1 in attached).

Real time attenuated total reflectance Fourier transform infrared (RT-ATR FTIR) spectroscopy with custom bottom-up irradiation16 was used to show a 5-8× higher polymerization rate upon exposure to green (530 nm), red (656 nm), or far-red (740 nm) light in these systems. Furthermore, fluorescence quenching studies suggested that photoexcited BODIPY dyes acted as electron acceptors (i.e., reductive quenching) for radical generation, which was also supported by a larger energetic driving force identified from cyclic voltammetry and density functional theory. Transient absorption spectroscopy confirmed the hypothesis that that the presence of “heavy atoms” (e.g., halogens) results in faster intersystem crossing rates, which corresponds to higher triplet yields and longer excited state lifetimes. The longer lifetimes are thought to improve photocatalytic efficiency by increasing the number of collisions that occur per photon absorbed between BODIPY in the excited state and an initiator. As a final demonstration, high resolution DLP 3D printing with a low-energy green LED was used to fabricate an object with a sophisticated geometry (octet truss) that is difficult or impossible to access using traditional manufacturing approaches.

(2) Developing Visible Light 3D Printing. Using commercial PRCs that absorb blue (470 nm, fluorescein derivative), green (530 nm, Eosin Y), and red (620 nm, porphyrin derivative) light, resins were optimized to photocure within 10 seconds (Figure 2a in attached). Key discoveries and developments include rapid photocuring from combined iodonium (donor) and borate (acceptor) co-initiators, resolution enhancements from visible light absorbing azo-dyes, and efficient optimization using a custom “resolution print” method. Specifically, a series of visible light absorbing azo-dyes were examined as effective panchromatic passive light absorbers, termed opaquing agents (OAs), which improved vertical resolution for all wavelengths examined. The use of a three component photosystem comprising the different PRCs with borate and diphenyliodonium co-initiators that acted as an electron donor and acceptor, respectively, enabled the catalytic nature by turning over the PRC from the excited state to a radical ion and back to the ground state (Figure 2a in attached). Resolution was optimized on a custom visible light DLP 3D printer by varying OA concentration and exposure time per layer with a method that enabled multiple exposure times/layer to be varied in one object. Optical profilometry revealed that cure-through could be precluded with the use of OAs, providing 25 μm vertical resolution, while lateral features as small as ~40 μm (x,y-resolution) were also demonstrated, rivaling state-of-the-art UV-based DLP systems (Figure 2b in attached). The OAs additionally enhanced reproducibility by widening the processing window prior to cure through from ~1 to ≥ 6 s.

The photopolymerization rates and times to gelation were characterized using RT-FTIR spectroscopy and photorheology, respectively. Both techniques had excellent temporal control, with an initial 10s dark period showing no conversion followed by gelation within a few seconds of turning the light ‘on’. Additionally, tensile testing of 3D printed acrylic dogbones indicated no significant difference in mechanical properties for samples prepared using violet, blue, green, or red light (Figure 3a in attached). The parts produces were also shown to be relatively isotropic in their mechanical response, indicating good adhesion between layers being printed. Versatility was highlighted by rapidly producing both rigid and extensible objects with stiffness ranging from ~1480 to 0.8 MPa. Finally, optimized resins were used to demonstrate high resolution printing of a hierarchical octet truss (Figure 3b in attached).

Training Opportunities: As part of the supported research efforts professional development at the postdoc, graduate, and undergraduate levels were accomplished. Technical experimental research skills were gained by all in the preparation of photocurable resins and light-based additive manufacturing. Additionally, the graduate students were trained in organic synthesis of chromophores used in photoredox catalysis. All researchers involved in the publications associated with the supported research gained valuable training in scientific writing, as the PI worked with them to put the publications together. Furthermore, skillsets in describing in words and displaying scientific information through figures and images was gained by the researchers during dissemination at group meetings.

Results Dissemination: Two publications in peer reviewed journals resulted from the supported research (DOI: 10.1021/jacs.0c07136 and 10.1021/acscentsci.0c00929), which was referenced in the acknowledgements section for each. Researchers working on the projects disseminated results periodically during private group meetings with the PI's group as well as during one-on-one monthly meetings and triweekly sub-group meetings. Dissemination of research was also accomplished at 4 conferences/workshops as part of invited talks: 15th International Conference on Polymers for Advanced Technologies (PAT) in August 2019, 258th American Chemical Society (ACS) Meeting in August 2019, 3M Technical Forum in September 2019, and Next Generation Smart Materials Workshop in December 2019.

Honors and Awards: Research supported by the present grant was highlighted on multiple occasions:

1) Chemical and Engineering News, a respected magazine in this general research area: Title - "For fast, high-resolution 3-D printing, visible light is gaining on UV" (link: https://cen.acs.org/materials/3-d-printing/fast-high-resolution-3-D/98/i36?utm_campaign=CENRSS&utm_medium=LatestNews&utm_source=LatestNews)

2) HepatoChem, a chemical company focused on light-based research: Title - "The 20 Must Read Photochemistry Papers from 2020" (link: https://e0e.327.myftpupload.com/the-20-must-read-photochemistry-papers-from-2020/)

3) The College of Natural Sciences at The University of Texas at Austin: Title - "20 Cool UT Science Stories from 2020 (Not about COVID-19)" (link: https://cns.utexas.edu/news/20-cool-ut-science-stories-from-2020-not-about-covid-19?utm_campaign=NASC_FY20-21_Newsletter_TexasScience-Jan2021_EML&utm_medium=email&utm_source=Eloqua)

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Pengtao Lu
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Partners

,

I certify that the information in the report is complete and accurate:
Signature:
Signature Date:

DESIGNING WAVELENGTH-SPECIFIC VISIBLE LIGHT PHOTOCURABLE RESINS

OVERVIEW. The research efforts supported under the army research office (ARO) short term innovative research (STIR) program, award number W911NF1910310, focused on the development of novel and efficient visible light photoredox catalysts (PRCs) to create polymer networks for the use-inspired purpose of emergent light-based additive manufacturing approaches. The long-term objective was to enable wavelength-specific photocuring, or solidification of liquid resins into solid objects, with spatiotemporal control. Of innovation was the development of novel boron dipyrromethene (BODIPY) PRCs that set a new record in low energy green, red, and far-red light photocuring (published in the *Journal of the American Chemical Society*)[1] and the implementation of a three-component photocatalytic process that enabled for the first time rapid high resolution visible light 3D printing (published in *ACS Central Science*)[2]. These fundamental scientific discoveries will pave the way towards more energy efficient additive manufacturing approaches that are amenable to multifunctional and multimaterial 3D printing via the use of wavelength-specific photocatalysis. Presented herein is a background on the problems studied along with the key results made possible by support from the ARO.

PROBLEM STUDIED. Light has been used to rapidly convert liquid resins into solid objects via photocuring, which has enabled transformative technological advancements in imaging, photolithography, adhesives, coatings, and, most recently, stereolithographic 3D printing.[3–9] However, in contemporary photolithography and more recently stereolithographic additive manufacturing, high energy UV/violet light (< 420 nm) is used to prepare 2D polymer patterns on surfaces and 3D objects, respectively. ***The reliance on UV light limits material compatibility due to degradation and attenuation by absorption or scattering of high energy photons.*** To solve this problem we turned to visible light as a more mild and cost-effective energy source for photocuring, which has been made possible by the recent widespread availability of inexpensive light emitting diodes (LEDs).[10–15] However, ***photocuring with visible light is an ongoing challenge that has been restricted to long exposure times (> 60 s) and/or high intensity irradiation (> 50 mW/cm^2)***, precluding their utility in photocuring applications.[10–15] The tradeoff between reaction rate and incident light intensity necessitated a closer examination of visible-light activated PRCs to advance state-of-the-art photocuring. Furthermore, translation of rapid visible light photocuring to emergent 3D printing technology represented an opportunity to examine the associated fundamental scientific challenges, such as the influence of resin composition and wavelength of light exposure on resolution and mechanical properties of the cured parts. These two unmet needs were examined through a systematic analysis of BODIPY PRCs and digital light processing (DLP) 3D printing with violet, blue, green, and red LEDs.

SUMMARY OF KEY RESULTS. Structure-property relationships as they pertain to efficient green-to-far red light absorbing BODIPY PRCs (**1**)[1] and rapid high resolution visible light-based DLP 3D printing with commercial PRCs (**2**)[2] were examined through the utility of novel three component photosystems. Through this approach, we have gathered the requisite capability and knowledge to facilitate the rational design of multimaterial 3D objects via wavelength-specific photocuring. Thus, ***the chemistry has informed the materials development, and the materials will enable unique capabilities for the objects they comprise*** (e.g., joints, actuators, synthetic tissue, and reinforced plastics) with potential utility in state-of-the-art camouflage and protective wear technologies of relevance to the ARO and more generally the Department of Defense missions.

(1). ***Structure-Property Relationships for Efficient Visible Light Photochemistry.*** Structure-property relationships of visible light activated PRCs that improve efficiency in photocuring were identified using BODIPY as a scaffold. *Key findings include rapid photopolymerizations (complete conversion within ~60 s) at extremely low catalyst loadings (~0.001 mol%) or light intensities (~0.01 mW/cm^2 green light or ~1 mW/cm^2 far-red light).* This was made possible by halogenation of the BODIPY core, which was demonstrated to be an effective strategy to improve photopolymerization efficiency across multiple BODIPY classes (both carbon and nitrogen bridged derivatives) (**Figure 1**).

Real time attenuated total reflectance Fourier transform infrared (RT-ATR FTIR) spectroscopy with custom bottom-up irradiation[16] was used to show a 5-8× higher polymerization rate upon exposure to green (530 nm), red (656 nm), or far-red (740 nm) light in these systems. Furthermore, fluorescence quenching studies suggested that photoexcited BODIPY dyes acted as electron acceptors (i.e., reductive quenching) for radical generation, which was also supported by a larger energetic driving force identified from cyclic voltammetry and density functional theory. Transient absorption spectroscopy confirmed the hypothesis that that the presence of "heavy atoms" (e.g., halogens) results in faster intersystem crossing rates, which corresponds to higher triplet yields and longer excited state lifetimes. The longer lifetimes are thought to improve photocatalytic efficiency by increasing the number of collisions that occur per photon absorbed between BODIPY in the excited state and an initiator. As a final demonstration, high resolution DLP 3D printing with a low-energy green LED was used to fabricate an object with a sophisticated geometry (octet truss) that is difficult or impossible to access using traditional manufacturing approaches.

(2) *Developing Visible Light 3D Printing.* Using commercial PRCs that absorb blue (470 nm, fluorescein derivative), green (530 nm, Eosin Y), and red (620 nm, porphyrin derivative) light, resins were optimized to photocure within 10 seconds (**Figure 2a**). *Key discoveries and developments include rapid photocuring from combined iodonium (donor) and borate (acceptor)*

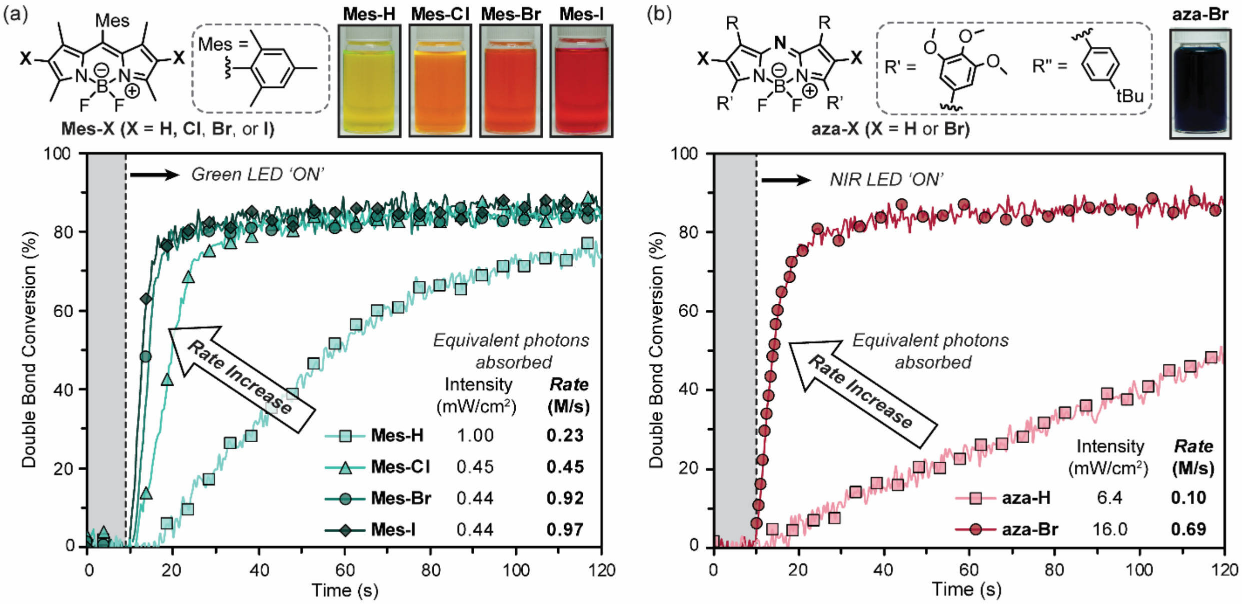

Figure 1. Effect of BODIPY halogenation on acrylate polymerization rates. (a) Comparing mesityl-BODIPY photoredox catalysts (PRCs) to polymerize isobornyl acrylate upon green light exposure (530 nm), while holding the photons absorbed constant. Real time attenuated total reflectance (ATR) FTIR spectroscopy was used to monitor double bond conversion, revealing a ~4× rate enhancement from Mes-H (non-halogenated BODIPY) to Mes-Br and -I. (b) Comparison of aza-BODIPY PRCs to polymerize isobornyl acrylate upon exposure to far-red light (740 nm). The aza-Br derivative resulted in an ~8× rate enhancement relative to aza-H, indicating that halogenation may be a universal strategy to improve PRC efficiency. Additional details can be found in Ref [1].

co-initiators, resolution enhancements from visible light absorbing azo-dyes, and efficient optimization using a custom "resolution print" method. Specifically, a series of visible light absorbing azo-dyes were examined as effective panchromatic passive light absorbers, termed opaquing agents (OAs), which improved vertical resolution for all wavelengths examined. The use of a three component photosystem comprising the different PRCs with borate and diphenyliodonium co-initiators that acted as an electron donor and acceptor, respectively, enabled the catalytic nature by turning over the PRC from the excited state to a radical ion and back to the ground state (**Figure 2a**). Resolution was optimized on a custom visible light DLP 3D printer by varying OA concentration and exposure time per layer with a method that enabled multiple exposure times/layer to be varied in one object. Optical profilometry revealed that cure-through could be precluded with the use of OAs, providing 25 µm vertical resolution, while lateral features as small as ~40 µm (x,y-resolution) were also demonstrated, rivaling state-of-the-art UV-based DLP systems (**Figure 2b**). The OAs additionally enhanced reproducibility by widening the processing window prior to cure through from ~1 to ≥ 6 s.

The photopolymerization rates and times to gelation were characterized using RT-FTIR spectroscopy and photorheology, respectively. Both techniques had excellent temporal control, with an initial 10s dark period showing no conversion followed by gelation within a few seconds of turning the light 'on'. Additionally, tensile testing of 3D printed acrylic dogbones indicated no significant difference in mechanical properties for samples prepared using violet, blue, green, or red light (**Figure 3a**). The parts produces were also shown to be relatively isotropic in their mechanical response, indicating good adhesion between layers being printed. Versatility was highlighted by

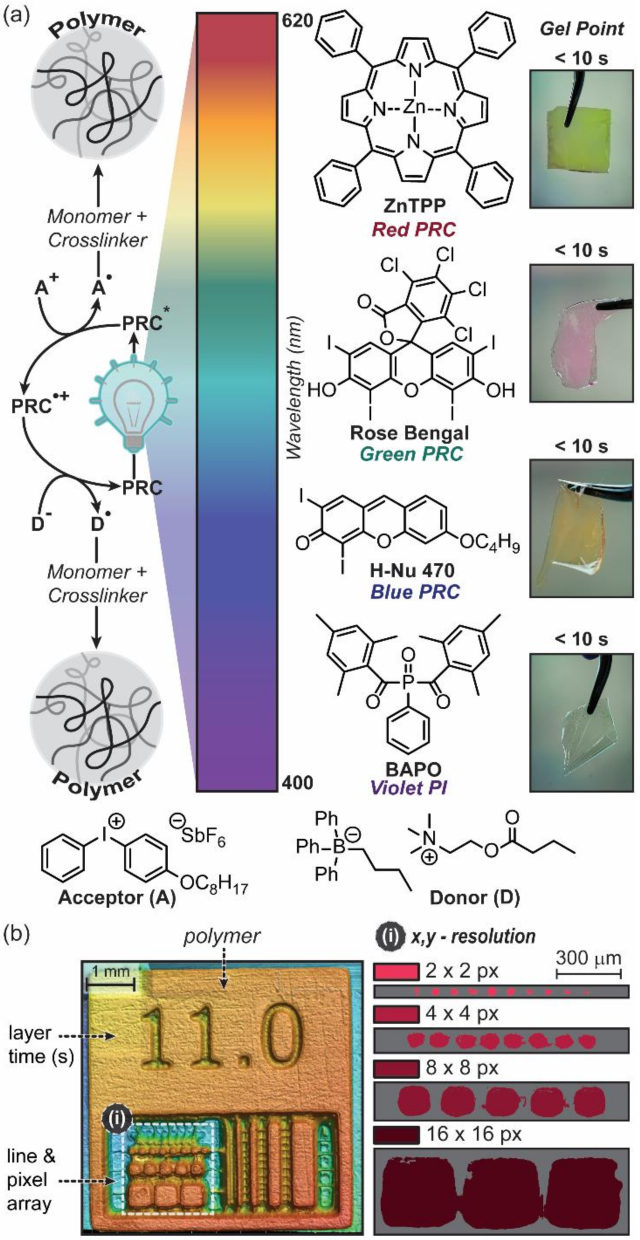

Figure 2. Resin optimization for high resolution visible light 3D printing. (a) General mechanism (oxidative quenching) for a three component system (left) and corresponding chemical structures of photoinitiator (PI) and photoredox catalysts (PRCs) used with violet (405 nm), blue (460 nm), green (525 nm), and red (615 nm) LED exposure and iodonium acceptor (A) and borate donor (D) co-initiators (center). Images to the right show thin films that were cured in <10 seconds using optimized resin formulations. (b) Optical profilometry image of resolution optimization red light 3D print (acrylic network) and corresponding surface analysis for 16, 8, 4, and 2 pixel wide squares (bottom right). Additional details can be found in Ref [2].

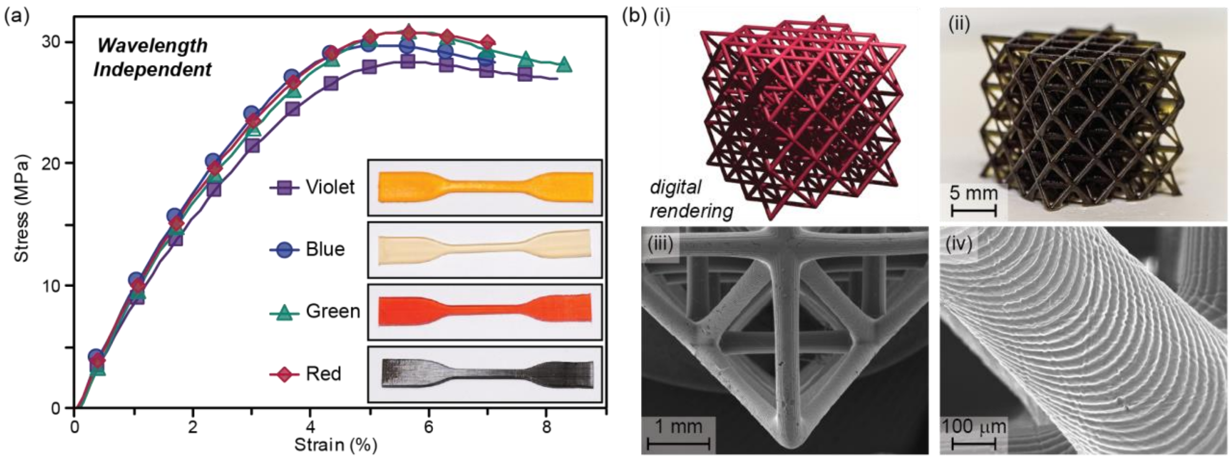

Figure 3. Characterization of visible light 3D printing. (a) Tensile testing of 3D printed dogbones showing wavelength independent mechanical properties for samples prepared with violet, blue, green, or red light. (b) Hierarchical octet truss as a complex 3D print demonstration. (i) Digital rendering, (ii) photograph of the printed object using red light, and (iii, iv) scanning electron microscope images showing the structural hierarchy. Additional details can be found in Ref [2].

rapidly producing both rigid and extensible objects with stiffness ranging from ~1480 to 0.8 MPa. Finally, optimized resins were used to demonstrate high resolution printing of a hierarchical octet truss (**Figure 3b**).

REFERENCES.

(1) Stafford, A.; Ahn, D.; Raulerson, E. K.; Chung, K. Y.; Sun, K.; Cadena, D. M.; Forrister, E. M.; Yost, S. R.; Roberts, S. T.; Page, Z. A. Catalyst Halogenation Enables Rapid and Efficient Polymerizations with Visible to Far-Red Light. *J. Am. Chem. Soc.* **2020**, *142* (34), 14733–14742.

(2) Ahn, D.; Stevens, L. M.; Zhou, K.; Page, Z. A. Rapid High-Resolution Visible Light 3D Printing. *ACS Cent. Sci.* **2020**, *6*, 1555−1563.

(3) Aguado, B. A.; Grim, J. C.; Rosales, A. M.; Watson-Capps, J. J.; Anseth, K. S. Engineering Precision Biomaterials for Personalized Medicine. *Sci. Transl. Med* **2018**, *10*, 8645.

(4) Camposeo, A.; Persano, L.; Farsari, M.; Pisignano, D. Additive Manufacturing: Applications and Directions in Photonics and Optoelectronics. *Adv. Opt. Mater.* **2019**, *7* (1), 1800419.

(5) Wallin, T. J.; Pikul, J.; Shepherd, R. F. 3D Printing of Soft Robotic Systems. *Nat. Rev. Mater.* **2018**, *3* (6), 84–100.

(6) Zhang, J.; Xiao, P. 3D Printing of Photopolymers. *Polym. Chem.* **2018**, *9* (13), 1530–1540.

(7) Jung, K.; Corrigan, N.; Ciftci, M.; Xu, J.; Seo, S. E.; Hawker, C. J.; Boyer, C. Designing with Light: Advanced 2D, 3D, and 4D Materials. *Adv. Mater.* **2019**, 1903850.

(8) Lim, K. S.; Galarraga, J. H.; Cui, X.; Lindberg, G. C. J.; Burdick, J. A.; Woodfield, T. B. F. Fundamentals and Applications of Photo-Cross-Linking in Bioprinting. *Chem. Rev.*

2020.

(9) Yu, C.; Schimelman, J.; Wang, P.; Miller, K. L.; Ma, X.; You, S.; Guan, J.; Sun, B.; Zhu, W.; Chen, S. Photopolymerizable Biomaterials and Light-Based 3D Printing Strategies for Biomedical Applications. *Chem. Rev.* **2020**.

(10) Dumur, F. Recent Advances on Visible Light Metal-Based Photocatalysts for Polymerization under Low Light Intensity. *Catalysts* **2019**, *9*, 736.

(11) Bagheri, A.; Jin, J. Photopolymerization in 3D Printing. *ACS Appl. Polym. Mater.* **2019**, *1* (4), 593–611.

(12) Corrigan, N.; Yeow, J.; Judzewitsch, P.; Xu, J.; Boyer, C. Seeing the Light: Advancing Materials Chemistry through Photopolymerization. *Angew. Chemie - Int. Ed.* **2019**, *58* (16), 5170–5189.

(13) Strehmel, B.; Schmitz, C.; Cremanns, K.; Göttert, J. Photochemistry with Cyanines in the Near Infrared: A Step to Chemistry 4.0 Technologies. *Chem. - A Eur. J.* **2019**, *25* (56), 12855–12864.

(14) Xiao, P.; Zhang, J.; Dumur, F.; Tehfe, M. A.; Morlet-Savary, F.; Graff, B.; Gigmes, D.; Fouassier, J. P.; Lalevée, J. Visible Light Sensitive Photoinitiating Systems: Recent Progress in Cationic and Radical Photopolymerization Reactions under Soft Conditions. *Prog. Polym. Sci.* **2015**, *41* (C), 32–66.

(15) Chatani, S.; Kloxin, C. J.; Bowman, C. N. The Power of Light in Polymer Science: Photochemical Processes to Manipulate Polymer Formation, Structure, and Properties. *Polym. Chem.* **2014**, *5* (7), 2187–2201.

(16) Allen, M. J.; Page, Z. A. Tracking Photocuring via ATR-FT-IR with Illumination through the ATR Element. *Spectrosc. Appl. Noteb.* **2020**, *35* (2), 78.